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RESIN/GRAPHITE FIBER COMPOSITES

by

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16. Abstract

Processing techniques were developed for the fabrication of both polyphenylquinoxaline and polyimide composites by the in situ polymerization of monomeric reactants directly on the graphite reinforcing fibers, rather than using previously prepared prepolymer varnishes. Void-free polyphenylquinoxaline composites were fabricated and evaluated for room and elevated flexure and shear properties. The technology of the polyimide system was advanced to the point where the material is ready for commercial exploitation. A reproducible processing cycle free of operator judgment factors was developed for fabrication of void-free composites exhibiting excellent mechanical properties and a long time isothermal life in the range of 288°C to 316°C. The effects of monomer reactant stoichiometry and process modification on resin flow were investigated. Demonstration of the utility and quality of this polyimide system was provided through the successful fabrication and evaluation of four complex high tip speed fan blades.

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FOREWORD

This document represents the final report of the work accomplished between 27 June 1973 and 26 September 1974 by TRW Incorporated for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio under Contract NAS3-17772 on Resin/Graphite Composites. This work was carried out under two different Project Managers in Dr. T. T. Serafini's group in the Materials and Structures Division. Mr. Morgan P. Hanson served first as Project Manager and the program was completed under the technical direction of Mr. Raymond D. Vannucci.

Work on the program was conducted at TRW Materials Technology of TRW Equipment, Cleveland, Ohio. Mr. W. E. Winters was the TRW Program Manager; the TRW Project Engineer was Mr. P. J. Cavano.

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SUMMARY

The objective of this program was to demonstrate the effectiveness of the in situ polymerization of monomer reactants (PMR) approach for fabricating polymer matrix composite fan blades. The program objective was accomplished by fabricating HT-S graphite fiber/PMR polyimide composite ultra-high tip speed fan blades. Studies performed in attaining the program objective included the fabrication and evaluation of PMR polyimide and polyphenylquinoxaline (PPQ) graphite fiber reinforced composites and the development of processing methodology for fabricating PMR polyimide fan blades.

The PPQ monomer solution was prepared by dissolving the tetracarbonyl and the tetraamino compounds in 1-methyl-2-pyrrolidinone at room temperature. The polyimide monomer solution was prepared by mixing an aromatic diamine and two ester-acids in methyl alcohol. In each case, these solutions were applied directly to graphite fiber to form the prepreg which was then dried and molded in a straightforward manner.

Experimental studies with the polyphenylquinoxaline system included the fabrication of panels that were evaluated for room and elevated temperature flexural and interlaminar shear strengths. The investigation of the polyimide matrix was more extensive and included the confirmation of thermo-oxidative stability, examination of a second formulated molecular weight polyimide, the testing of composites prepared by a number of alternate cycles and the fabrication of four void-free ultra-high tip speed fan blades by the preferred processing cycle.

The PMR approach with both matrices was found to provide excellent processability. Void-free components were repetitively produced with both systems. However, it was concluded that the PPQ matrix system requires additional work to eliminate the thermoplasticity encountered in elevated temperature testing of composites before postcure.

Results of the effort with the PMR polyimide were very gratifying, and it is felt that the system is ready for immediate commercial application. The use of freshly prepared benzophenone ester-acid completely eliminated a previous problem with voids, and the material was found to yield void-free laminates with a number of different processing cycles. Composites prepared with the preferred cycle, which obviates the need for operator judgment, were found to have excellent isothermal resistance and mechanical properties at both room and elevated temperatures. Isothermal data indicated that the matrix is suitable for long time use (ca. 1000 hours) in the range of 288°C to 316°C. Prepregging, layup, solvent removal and imidization were accomplished safely and easily. Experimentation with an alternate formulated molecular

weight composition indicated that resin flow characteristics can be controlled in this manner as well as by variations in processing conditions. The fabrication of four high tip speed fan blades, some of which were service tested, resulted in void-free components capable of meeting the design requirements.

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1.0 INTRODUCTION

This document constitutes the final report on NASA-Lewis Contract NAS3-17772, initiated 27 June 1973, and describes the work performed between that date and 26 September 1974. The objective of the program was to demonstrate the effectiveness of the in situ polymerization of monomeric reactants approach for fabricating polymer matrix fan blades. The program objective was accomplished by fabricating graphite fiber/PMR polyimide composite ultra-high tip speed fan blades. The polymerization of monomeric reactants (PMR) approach was originally developed by NASA-Lewis personnel (1)(2) and provides a number of very real advantages that were described previously (3). Some of these advantages include: the use of a non-toxic solvent, such as methyl alcohol; elimination of prepolymer instability and aging characteristics; greater flexibility in resin constituent selection and processing responses; and greater process and property reproducibility.

The program was divided into three basic tasks which are described below:

TASK I - DEVELOPMENT OF PRELIMINARY PPQ PROCESSING TECHNIQUES BY THE PMR METHOD

The purpose of this task was to define preliminary processing techniques for the preparation of graphite fiber/PPQ composites and to conduct laminate evaluation.

TASK II - OPTIMIZATION OF PMR POLYIMIDE RESIN PROCESSING TECHNIQUES AND CHARACTERIZATION OF THE MOLDED COMPOSITES

In this task, optimized processing techniques were developed for the molding of void-free PMR-15 polyimide composites and mechanical and thermo-oxidative characterization performed on the fabricated laminates.

TASK III - PREPARATION FOR AND THE MOLDING OF HIGH TIP SPEED FAN BLADES

In this phase of the program, the processing methods developed in Task II were applied to the molding of four complex graphite fiber/PMR resin fan blades using the design and tooling developed on contract NAS3-15335. Quality determinations were made of the four blades and some preliminary data collected on the spin performance of the fabricated components.

The PMR approach to the chemistry and processing of advanced resin matrices was found to be valuable, significant and worthy of continued attention in both development and commercial situations. The PMR polyimide was found to be safe, easy to handle, processable with relatively wide processing limits, and suitable for the fabrication of complex hardware components. The PMR polyphenylquinoxaline system was found to process easily but requires further development effort. Details of the materials, processing techniques employed, evaluation methods and results are described in the body of the text.

2.0 POLYPHENYLQUINOXALINE COMPOSITES

Currently, the use of a PPQ matrix requires the application of an extremely viscous, low solids solution of the polymer in m-cresol to the fiber reinforcement. A high viscosity solution provides poor fiber wetting and results in an uneven distribution of the polymer on the fiber. The PMR approach permits the use of a high solids solution, facilitates fiber wetting, and eliminates the need for prior polymer synthesis. It is clear then that the PMR approach is a valuable one, and for the reasons mentioned, a preliminary processing development program was undertaken.

2.1 Composite Constituent Materials

In the following paragraphs, details of the program fiber choice as well as the monomeric reactant characteristics and the reactant solution behavior will be given.

2.1.1 Reinforcing Fiber

Published literature (3)(4) has recorded the thermo-oxidative attack sustained at 316°C (600°F) by the "high strength" graphite fibers vs. the "high modulus" type. Since one of the objectives of the program was to evaluate a high temperature PPQ resin matrix, it was decided to employ the "high modulus" type reinforcement to avoid any possible masking of high temperature isothermal behavior of the test composites. Specifically, the primary material chosen was Magnamite HM-S tow from Hercules Incorporated, Wilmington, Delaware. This material is a continuous, 10,000 filament tow material. The fiber was surface treated but carried no sizing or finish.

2.1.2 Monomeric Reactants

The specific compounds used to prepare the PPQ system are shown below.

Material	Abbreviation	Source
3, 3', 4, 4' - tetraaminobenzophenone	TAB	Burdick & Jackson
4, 4' oxydibenzil	ODB	Research Organic/Inorganic
1-methyl-2-pyrrolidinone (practical)	NMP	Eastman Kodak

Vendor certifications indicated that the ODB had a melting point range of 107-108°C, while the TAB melting point range was from 216-218°C.

The tetraaminobenzophenone and the oxydibenzil were mixed in a 1:1 molar ratio to provide a 30 w/o solids solution. This was accomplished by dissolving each component separately in NMP and then combining the two solutions. Viscosity after combination was 88 $N \cdot s/m^2$ (88 cps) and the solution specific gravity was 1.14.

2.2 Processing Procedures

Using the solution described above, prepreg was prepared and laminates molded. The following paragraphs describe the techniques used.

2.2.1 Impregnation

Impregnation of the fiber was carried out by dry winding the fiber on a 50.8 cm (20 inch) diameter drum and then metering the resin solution onto the fiber surface with a peristaltic pump. The number of tows per inch (N) was calculated with the following equation.

$$N = \frac{T\ V_f\ \rho_f}{W}$$

where: N = number of tows per inch
T = thickness per ply
V_f = fiber fraction
ρ_f = fiber density
W = fiber weight per unit length

Figures 1 through 3 illustrate the technique and equipment used for impregnation. Figure 1 shows the winding apparatus. The tow is wound with a slight tension created by an electrically operated spool brake. The roller and hoop arrangement shown spread the 10,000 filament tow so that an even fiber placement was achieved. Figure 2 shows the resin solution reservoir and the peristaltic pump. The pump metering rate was correlated with the traverse speed of the head on the Edwards Wrapping Machine. In this way, the required, calculated amount of resin was deposited in one pass on the fiber surface. Figure 3 shows the technique used to effect the initial drying or devolatization process carried out prior to removal of the prepreg from the drum. The six infrared lamps (250 watts each) were on 17.8 cm (seven inch) centers and 15.2 cm (six inches) from the surface of the fiber. The IR lamps were used for a total of 1-1/2 hours. The material at the end of this time had excellent tack, drape and collimation. Volatile checks indicated a total volatile content range of 21.0 to 23.1 w/o. The volatiles materials were removed through an overhead hood mounted over the winding area of the machine. Prepreg thickness calculations were based on obtaining a finished molded ply thickness of 0.254 mm (0.010 inch) and a fiber volume of 55 to 60 percent.

2.2.2 Molding

A number of 5.1 x 15.2 cm (2 x 6 inch) unidirectional HM-S laminates were molded at 6.9 MPa (1000 psi) at 316°C, 330°C and 343°C (600°F, 625°F, 650°F) with various dwell times (before pressure application) ranging from 15 to 90 seconds. All laminates were ultrasonically inspected with a permanent C-scan record and reviewed for surface quality. Sonic traces of only two laminates exhibited the presence of defects. These two were molded at 330°C (625°F) with dwell times of 15 and 30 seconds. It seems clear that the short dwell times were inadequate to permit volatilization of all of the NMP before full molding

pressure was applied.

It should be noted that, when the laminates were inserted at or above 316°C (600°F), a brief fire ensued in the press in the immediate vicinity of the platens during the dwell period. This is obviously due to the emission of the NMP. The literature indicates that the autoignition temperature for the NMP material is 346°C (655°F). The reason for the autoignition of the NMP expelled from the die at 316°C is unknown.

The other criterion, besides the C-scan, used for selection of process parameters was surface quality. Surface indications observed included: pock marks, uniform surface roughness and slight local roughness at the ends of the laminates. Considering these indications as well as the attendant sonic trace, the recommended dwell times before pressure application for the three temperatures were as follows:

316°C (600°F)	75 sec
330°C (625°F)	60 sec
343°C (650°F)	30 sec

It is felt that some latitude (perhaps ±10 seconds) exists in these selected dwell times, and it is expected that some variation might be required in succeeding moldings depending on laminate volume, prepreg volatile content and age of prepreg (relative advancement). Little resin flow was observed with any of these cycles so this factor was not considered in making final selections. If a single cycle were to be chosen, it is recommended that the 75 second dwell time at 316°C be selected. This is based on the visual quality of the laminates, the fact that a 75 second dwell time does not demand the rapid operator response time of the 30 second hold and finally because it is felt that the lower the initial cure temperature the better from the standpoint of residual stresses created by thermal differential growth and shrinkage.

2.3 Composite Properties

To obtain some knowledge of the mechanical properties of this type laminate, three panels were selected for flexural and short beam shear testing at room temperature and 316°C (600°F). The three panels chosen were prepared as shown in the following table and tested in the unpostcured condition.

Panel No.	Insertion Temp., °C	Dwell Times sec.	Hold at Temp.	Pressure MPa (psi)
669-31	316	30	30 min/316°C	6.9 (1000)
669-53	343	30	30 min/343°C	3.4 (500)
			30 min/371°C	3.4 (500)
669-81	316	75	60 min/316°C	6.9 (1000)

The test values from specimens taken from these laminates are shown in table I. As can be seen, the room temperature properties are quite reasonable; however, the elevated temperature properties are obviously poor. It is clear

from an examination of the high temperature specimens and the collected data that the unpostcured PPQ resin matrix displayed a thermoplastic behavior which resulted in inferior elevated temperature properties.

Additional studies with the PPQ system were terminated so that a more intensive effort could be applied to the development of the polyimide resin formed by the PMR approach.

Two other additional items are of interest in the characterization of the PPQ system. Two specimens of the PPQ were cast without reinforcement and slowly brought to 316°C and cooled. Visually, the samples appeared void-free. Water displacement measurements of specific gravity of these samples, and back calculations on small samples of cured composites with a known resin content, were conducted to determine the cured resin specific gravity. The value determined was 1.24. This value should be used in calculating fiber fractions and void contents of composites in subsequent work with this system.

Cured PPQ prepreg was chemically analyzed for resin content using the H_2SO_4/H_2O_2 extraction method based on Haynes and Tolbert (5) work which investigated epoxy, phenolic and polyimide resins on graphite fibers. Good correlation was obtained between calculated and determined resin content values; therefore, this technique was deemed suitable for use in subsequent investigations with the PPQ resin system.

2.4 Sub-Task Summary and Recommendations

Monomer solution mixing was easily achieved in a safe solvent, NMP, and at relatively high concentration of 30-35 w/o. Subsequent prepregging was straightforward and the resulting prepreg could be easily devolatilized to yield a material with excellent tack and drape characteristics. Storage in a sealed container at room temperature for times up to three weeks did not seem to affect moldability. Two problems encountered in molding included: 1) the possibility of autoignition of the initially evolved NMP unless auxiliary measures are taken to transport or dissipate these fumes and 2) the limited flow observed with the mold cycles evaluated. Multiple C-scan evaluations of molded panels revealed essentially void-free composites produced by a molding process including preform insertion into a hot die (316°C-343°C) with dwell times ranging from 75 seconds to 30 seconds before application of the molding pressure of 6.9 MPa (1000 psi). Preliminary mechanical property evaluation revealed excellent room temperature values but inferior strength at 316°C on unpostcured specimens. This type of performance and an examination of the tested specimens indicates an inherent thermoplasticity which, while a common characteristic of quinoxaline polymer systems, represents an area where further work should be directed. Efforts were not made to solve these problems during the course of this program, but it is felt that the encouraging results obtained in the solution and prepreg handling of this difficult system represent significant advancements.

3.0 POLYIMIDE COMPOSITES BY THE PMR APPROACH

The major portion of the program effort was devoted to the investigation of polyimide resin via the polymerization of monomeric reactants (PMR) approach. The following sections will describe the experimental work performed and briefly recount a little necessary history. To simplify the need for a full repetitive designation of the material as a "polyimide fabricated by the PMR approach," the system will be identified as PMR. The bulk of the work was performed with a 1500 Formulated Molecular Weight (FMW) system. Therefore, the system is identified as PMR-15. In the case of other Formulated Molecular Weights, the first two digits are used in a similar way; e.g., an 1100 FMW system would be described as a PMR-11.

3.1 Status Review

Previous work (1)(3) has established that the PMR-15 system fulfilled many of the originally anticipated advantages. It was found that solution preparation, prepregging, layup and imidization were safe and straightforward. The preparation of laminates could be accomplished with a number of different cycles and the resultant composites were thermally, oxidatively and hydrolytically stable. Tests indicated that the composite material had a short-term useful life at 316°C (600°F) to 343°C (650°F) and a long-life temperature limit in the 288°C (550°F) to 316°C (600°F) range. However, at the conclusion of the work described in NASA CR-121275 (reference 3), two quality related problems were still not fully resolved. These were surface imperfections and a nominal void content of 1 to 3 v/o. Numerous processing variations did not completely eliminate these problems and further work was deemed necessary. Additional effort, described in this document, did provide a complete solution to any remaining problems of the type identified.

3.2 Identification of Raw Material Problem

The monomeric reactant solution for the PMR is prepared by mixing a diamine and two ester-acids in methyl alcohol. The specific compounds used in the work in reference 3 and in the early portion of the current effort are shown below:

Material	Abbreviation	Source
Monomethyl ester of 5-Norbornene-2, 3-dicarboxylic acid	NE	Burdick & Jackson
Dimethyl ester of 3, 3', 4, 4' - benzophenonetetracarboxylic acid	BTDE	Burdick & Jackson
4, 4' - methylenedianiline	MDA	Eastman Kodak
Methyl alcohol (absolute)	-	Fisher

The BTDE was received, stored and used as an 85 w/o solution in methyl alcohol; the other two compounds are free flowing powders. Acceptance criteria included moisture content, melting point and infrared spectroscopy; no material deviations were identified.

Considerable effort during the early portion of this program was expended on examining alternate processing conditions to eliminate voids in the finished laminates. These efforts were unsuccessful. Studies conducted at NASA Lewis Research Center revealed that void-free composites could be easily fabricated using freshly prepared BTDE rather than the commercially obtained material (6). Impurities, perhaps tri- and/or tetra-esters, were probably responsible for the difficulties. After the adoption of the modification, i.e., the use of freshly prepared BTDE, absolutely no evidence of the previously encountered surface imperfections or void problems was experienced.

3.3 Composite Processing

The sections below describe in detail the experimental effort expended in preparing and characterizing the PMR polyimide resin matrix composite, using the freshly prepared BTDE. Much of the work involved the use of the HM-S fiber. Data are also reported for composites fabricated with the Magnamite HT-S reinforcement.

3.3.1 Solution Preparation

The 1500 formulated molecular weight solution was prepared using the following mole ratios of the monomeric reactants:

Material	Mole Ratio
NE	2.000
MDA	3.087
BTDE	2.087

The BTDE was prepared by refluxing benzophenonetetracarboxylic dianhydride (BTDA) with an excess of anhydrous methyl alcohol for a period of two hours after initiation of boiling. The BTDA was purchased commercially; the material was procured from Aldrich Chemical Company, Incorporated and is described as 96% pure with a two degree (^{o}C) melting point range. Esterification calculations were conducted on the basis of a 100% BTDA content and excess alcohol was added in sufficient quantity to yield a final 50 w/o solution of BTDE in methyl alcohol. Refluxing was accomplished in a 1000 ml flat-bottom glass reaction kettle (side walls insulated) positioned on the platform of a heated magnetic stirring device. In this way, mechanical agitation of the solution could be maintained continuously during reflux.

After cooling of the BTDE solution, it was mixed with a previously prepared 50 w/o solution of 4, 4' methylenedianiline (MDA) and monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid (NE) in methyl alcohol. After mixing, the complete monomer solution (1500 formulated molecular weight) was ready for use in impregnating the reinforcement. The 50 w/o solution of the PMR-15 had a specific gravity of 1.000 and a viscosity in the range of 40 $N \cdot s/m^2$ (40 cps).

3.3.2 Fiber Impregnation

Using the 50 w/o solution prepared, all prepreg was made up by dry winding the fiber and impregnating with the use of a peristaltic pump as discussed in paragraph 2.2.1.

Tack and drape were controlled by drying procedures. With appropriate procedures, both these characteristics were completely satisfactory. The exposure under the infrared lamps for one hour, after a 15 minute exposure at room temperature, brought the total volatile content to 13.0 to 16.0 w/o. The prepreg was still too "wet" at this point and a further devolatilization in an air-circulating oven for 10 minutes at 82°C (180°F) brought the volatile content down to 8 to 11 w/o which was felt to be the correct level for best handleability in preparing flat test panels.

3.3.3 Solution and Prepreg Stability

While it was planned to routinely esterify BTDA, prepare a monomer solution, impregnate fiber and use the prepreg in a repetitive, small-batch manner with minimum delay in the sequence, it was felt that some preliminary knowledge of storage limits would minimize waste and forestall questions in subsequent experimentation. For this reason, three short-time storage conditions were investigated. These included:

a) Storage of the BTDE solution alone for 15 days.

b) Storage of the complete monomeric solution for 16 days.

c) Storage of prepreg for 28 days.

In each case, the criteria used were panel surface appearance and ultrasonic C-scans of the final composites. A control panel was first prepared by esterifying, mixing the complete monomer solution, prepregging and molding within a two-day period. The panel displayed a good surface and the C-scan was free of defect indications. The C-scan technique employed was the identical one developed and used on a prior program (3) so that direct correlation with previous quality data could be made. This laminate was prepared by imidizing for one hour at 204°C (400°F) in an air-circulating oven and then placing the imidized stack in a die preheated to 232°C (450°F), holding for 10 minutes and then applying 6.9 MPa (1000 psi) and raising the temperature to 316°C (600°F). The laminate was held at this temperature for one hour and cooled to room temperature. These processing conditions and the resultant C-scan represent a temporary control standard against which aged materials were measured.

In the first experiment, the required quantity of 50 w/o BTDE was prepared and stored in a sealed container at room temperature for 15 days. At the end of this time, it was mixed with a fresh MDA/NE solution and a prepreg prepared and molded with the same cycle used on the control. The quality of the surface and the C-scan was equivalent to the control panel, leading to the conclusion that, as a minimum, the 15 day storage of the 50 w/o BTDE solution was acceptable.

The next trial was an evaluation of the complete monomer solution stability. A freshly prepared batch of BTDE was prepared and immediately mixed with the MDA and NE components and stored at room temperature in a sealed container for 16 days. At the end of this time, a prepreg was prepared and a laminate molded. Again, the quality of the panel surface and the C-scan was equivalent to the control. Since no visual change was observed in the monomer solution and the

results of the C-scans were favorable, it can be concluded that a 16-day hold at room temperature, without the presence of moisture, does not degrade the performance of the monomer solution.

In the third test, a freshly prepared batch of BTDE was used to make up a new solution of monomers which was immediately applied to the reinforcing HM-S fiber. This prepreg was stored uncovered in a laboratory ambient environment for 28 days before being molded under the same conditions as each of the other aging panels. As might be expected, the prepreg had lost tack and drape, but the resultant laminate exhibited the same type of surface and the C-scan displayed no defect areas. It was, therefore, concluded that the 28-day storage period, while yielding a material without drape and tack, did not adversely affect the ability of the prepreg to be molded into a high quality laminate.

In summary then, three storage experiments were performed which established initial boundaries for BTDE, the monomer solution and the prepreg. The results indicated that excellent laminates were obtained within periods of time felt to be representative of good practice. Further experimentation would most likely extend these first limits.

3.3.4 Process Optimization Studies

In the stability trials, it was noted that only trace amounts of resin flow were obtained, although excellent consolidation was achieved. Under certain circumstances of hardware design and fabrication, a higher amount of resin expulsion is sometimes deemed desirable. A series of experiments was therefore designed in an attempt to achieve higher resin flow as a means of controlling molded component ultimate thickness.

3.3.4.1 Flow-During-Imidization

A first experiment involved consolidation during the imidization process. Ten unidirectional plies of material were stacked in a cold die and molding stops were installed. The prepreg was prepared to yield 0.254 mm/ply (10 mils/ply); the molding stops were deliberately set for a 2.3 mm (90 mil) gap, i.e., 0.254 mm (10 mils) less than the predicted optimum. This was done to simulate a typical condition in close tolerance molding where an excess of material can be encountered and molding to a specific size is required.

The unimidized preform was installed in a cold mold between cold platens and contact pressure applied. The temperature was set for 204°C (400°F). When the laminate reached approximately 102°C (215°F), copious flow was noted. The laminate was held on the molding stops for 45 minutes at 102°C and then raised to 316°C (600°F) and held an additional 45 minutes with the stops still in place.

The laminate made in this way had a smooth and uniform surface and was to the predicted size. The sonic C-scan, however, exhibited a heavy defect pattern in the center with perhaps 1 to 1-1/2 cm of sound material around all four sides of the 10.2 x 20.3 cm (4 x 8 inch) laminate. While this laminate did come to the predicted size, it was reasoned that, with the punch on stops during the final curing period, the laminate itself was not receiving full or

adequate pressure. For this reason, two more laminates using the pressure during imidization technique were attempted.

In the next trial, the same procedure as described above was employed until the end of the imidizing cycle at 204°C. At this point, instead of leaving the stops in place, they were removed and the full 6.9 MPa (1000 psi) applied to the laminate, and the temperature raised to 316°C. The sonic C-scan on this panel was much improved but still showed a large area in the center containing voids. Additionally, the laminate thickness was 0.2 mm (8 mils) undersize.

A final trial was attempted in which the molding stops were adjusted to accommodate the added 0.2 mm thickness change. The same procedure was followed in preparing the laminate, and again, the stops were removed and the full pressure applied to the laminate. The finished laminate was to the correct size; an average thickness of 23 mm (89-1/2 mils). The C-scan, shown in figure 4, displays the same defect pattern in the center of the panel.

At the conclusions of these trials, work in this area of flow-during-imidization was temporarily suspended so that further effort on more orthodox alternate imidization/molding cycles might be pursued. While these limited, preliminary attempts did yield a C-scan with some defects, it is felt that the basic approach should be regarded as a potentially viable technique. The trials did demonstrate a useful characteristic of the system that might be found important in subsequent molding studies or in special fabrication circumstances.

3.3.4.2 Flow vs. Imidization

Next, a series of trials were completed using various oven imidizing temperatures with a subsequent insertion into a hot tool. The objective was to identify an imidizing-molding cycle that would produce sound laminates, as determined by sonic C-scan, with some reasonable amount of flow. In these first trials, two different die insertion temperatures were evaluated, 232°C (450°F) and 316°C (600°F).

Five different oven time/temperature cycles were employed with the 232°C die insertion temperature (all of which included a 10 minute hold before application of 6.9 MPa (1000 psi)). These oven imidizing conditions included:

121°C (250°F) for 8 hours

163°C (325°F) for 1 hour and 2 hours

191°C (375°F) for 1/4 hour and 1/2 hour

All of these panels displayed a good sonic trace, but resin flow was determined to be in the one percent or less range. Flow is calculated as the weight of resin flash divided by the original weight of the laminate.

In order to explore the 316°C die insertion temperature conditions, two small test matrices were prepared and completed. One employed a 121°C (250°F) imidization temperature and the other a 149°C (300°F) imidization temperature.

Both of the matrices are displayed in table II, with the weight percent flow recorded in the body of each test matrix table. As can be seen, quite reasonable quantities of resin flow were obtained with the 121°C imidization when coupled with the 30 second dwell time before pressure application. The 60 second dwell with these same imidization conditions yielded a much smaller amount of flow. The conclusion here seems to be that the extended 60 second time at 316°C completely, or nearly completely, imidized the resin, leading to reduced flow. In the second matrix, with an imidization at 149°C, much lower flow was realized, even with the 30 second dwell. It is important to note that all of the laminates described by both test matrices displayed excellent sonic C-scans.

After reviewing all of the results obtained from the various imidization/die insertion temperature experiments, it was clear that acceptable flow was achieved by a very moderate preheating cycle (imidization) before final pressure and chain extension temperatures were applied. While not confirmed by in-house analytical studies, it seems reasonable to hypothesize that the low temperature imidization cycles yielded a part in an incompletely imidized condition. This incomplete imidization apparently permitted matrix movement before an increased temperature limited this movement by completing the cyclization of the imide ring structures. However, the amounts of volatile condensation products were insufficient to induce perceptible void contents in the composites.

As a result of this reasoning, an examination was made of other molding conditions coupled with a low temperature imidization. Table III summarizes the results of a number of molding experiments in which laminates were oven-imidized at 121°C (250°F) for three hours and then inserted into a preheated die for various dwell times before pressure application and increase to 316°C (600°F). A series of prepreg samples (8 from 4 different prepregs) were checked for remaining total volatile content after the three-hour imidization; the range was from 1.5 w/o to 2.8 w/o with an average of 2.0 w/o. This material represented the partially imidized preforms charged into the die.

As can be seen from table III, significant quantities of flow were obtained at the higher insertion temperatures of 288°C (550°F) and 316°C (600°F) with 30 second dwell times. Even out to 90 seconds at 288°C (550°F), a flow of 4% was observed. It should also be emphasized that the sonic traces of these laminates displayed no unacceptable void concentrations. It was also observed that at the lower temperatures considerable discoloration of the panel surfaces occurred. This roughly corresponded to the percent defect area shown by sonic investigation. A review of these data seemed to indicate that to obtain maximum flow, along with a good sonic pattern and surface condition, a die insertion temperature of 288°C (550°F) should be used.

These experiments indicated that high flow and sound laminates, as determined by ultrasonic inspection, were obtained with the PMR-15/HM-S system when the material was imidized three hours at 121°C (250°F) and molded by inserting the preform into a die preheated to 288°C (550°F) with a 30-90 second dwell period before application of the 6.9 MPa (1000 psi) pressure and increase of the temperature to 316°C (600°F). To determine how long the resin remained in a formable or flowable condition at the 288°C temperature (in order to maximize that period of time during which part consolidation might occur),

two laminates were molded as above with a 60 second dwell at 288°C before application of the 6.9 MPa pressure and held at this temperature until the resin was observed to harden. This occurred after 10 minutes with one laminate and after 12 minutes with the second.

To identify any deleterious effects on mechanical properties that might be encountered with the extended hold period at 288°C, as opposed to the more orthodox cycle, room temperature and 316°C shear and flexure properties were checked on two laminates from the same prepreg and processed as shown below:

	Lam. 672-73	Lam. 672-74
Imidize	3 hr/121°C	3 hr/121°C
Insertion Temperature	288°C	288°C
Dwell Time	60 sec	60 sec
Pressure	6.9 MPa	6.9 MPa
Hold before Temperature Raised to 316°C	1 hour	0
Time at 316°C	1 hour	1 hour
Final Postcure Temperature	343°C	343°C

Sonic inspection revealed clean C-scans in each case, and as can be seen from table IV, the data were directly comparable, indicating no significant difference between these two cycles. In comparing these data to properties collected with other processing cycles, the flexural strength and modulus values were in the same family. The shear values, however, were significantly lower than previously seen.

In considering this lowered shear performance, it should be noted that a number of unidirectional laminates prepared with the 288°C cycle were observed to have cracked after withdrawal from the mold. This latter behavior might be construed to reflect a lower transverse tensile strength since the cracking was not seen with panels prepared with a 316°C insertion temperature. The lower shear values and suspected low transverse tensile values were felt to be related. For these reasons, as well as the surface discoloration sometimes observed with the 288°C insertion cycle if dwell times were too short, further experimentation with this cycle was discontinued. The establishment of this modified technique, with preliminary process limits, was of value since it provides a method which might find utility in specific applications with particular part configuration, reinforcement types, or equipment characteristics.

Since a number of different process cycles were being investigated, with regard to flow and sonic characteristics, it was decided that some knowledge of the mechanical properties produced by these varying cycles should be determined. A limited test matrix, shown in table V, was devised to compare a number of parameters using flexural and shear strength as criteria. First, two completely different molding cycles, with die insertion temperatures of 232°C (450°F) and 316°C (600°F), were evaluated. In addition, laminates were

tested before and after postcure, and a number of different imidization times and temperatures were included in the matrix. As was noted previously, moderate (121°C) imidization conditions, coupled with a 316°C (600°F) die insertion temperature, produced significant flow (avg. 6.7 w/o). The single laminate, 672-5, introduced at 232°C into the die, had a flow of only 1%.

As can be seen from the data shown in table V, all values, with the exception of the portion tested at 316°C without postcure, were quite good. All of the imidization cycles evaluated with the HM-S reinforcement were satisfactory and that both molding processes produced good mechanical properties with good retention, after postcure, at elevated temperature. The lower flexural strength displayed by the postcured laminate from the 232°C cycle, compared to the postcured laminate from the 316°C cycle, might be attributable to the lower fiber volume of the laminate from the 232°C cycle. To summarize, excellent mechanical properties at both room and elevated temperature were obtained with the PMR-15/HM-S system under the different processing conditions studied, demonstrating the broad versatility of the system.

3.3.4.3 Fiber Surface Effects

All the data reported so far have been based on composites prepared with HM-S fiber. It was thought important to gain some knowledge of the response of the HT-S tow with the PMR-15 material. Initial experimental trials in molding seemed to indicate that the HT-S fiber laminates were exhibiting more flow than previously observed HM-S laminates processed with the same imidization and molding conditions. To confirm this, four laminates (two HT-S and two HM-S) were prepared using two different cycles. These process cycles are shown below, along with the w/o flow obtained. Sonic C-scans are shown in figures 5 and 6.

Process Cycle #1		HM-S	HT-S
Oven Imidization:	3 hr/121°C	Lam. #701-13	Lam. #701-9
Insertion Temp.:	288°C	Flow: 9 w/o	Flow: 14 w/o
Dwell:	30 sec		
Pressure:	6.9 MPa		
Hold before Set for 316°C:	15 min		
Time at 316°C:	1 hour		

Process Cycle #2			
Tool Imidization:	4 hr/121°C	Lam. #701-14	Lam. #701-12
Insertion Temp.:	316°C	Flow: 1 w/o	Flow: 9 w/o
Dwell:	60 sec		
Pressure:	6.9 MPa		
Time at 316°C:	1 hour		

As can be seen from the data, the HT-S reinforced laminates yielded significantly higher flow with the same process cycles when compared to the HM-S material. An examination of figure 5, comprising C-scans from HT-S and HM-S laminates, graphically displays the difference in response of the two fibers. It is felt that these differences reflect the altered behavior of the

HT-S fiber in imidization. It was hypothesized that more reactive sites on the HT-S, as reflected in commonly observed higher shear values, might account for this difference. For example, perhaps reactive sites on the fiber preferentially react with the matrix, thus initially limiting the imidization rate.

Photomicrographs also revealed the fact that some of the fiber from this lot of HT-S responded differently to the standard metallographic polishing techniques. This matter was discussed in detail with the fiber supplier, Hercules, and ultimately, they indicated that the difference in polishing was caused by inadequate washing of the fiber after the surface treatment step. They indicated that this operation is now under control and is no longer a problem; the fiber lot used was apparently made by Hercules in January of 1973.

This difficulty with the fiber is mentioned because work on the next lot of HT-S fiber revealed a flow behavior very similar to that initially observed on HM-S fiber. That is, the fiber showed the same minimum flow as noted with the first experiments with HM-S fiber. This behavior was again discussed with Hercules from the standpoints of surface area and the presence of reactive sites. The discussion revealed that measurements were not made of surface area; this could be of potential interest since a rough, high-area surface could reduce resin movement in molding. The question of reactive surface sites remains a moot point since no definitive data are available to indicate the absence or presence of these sites. If surface treatments produce these reactive sites, it seems conceivable that the rate of a chemical reaction (imidization or cure) occurring at the surface could be altered by the presence of these sites.

This fiber surface problem caused some consternation when first encountered. For example, table VI lists HT-S laminates prepared with various cycles to define optimum conditions. The wide disparities observed in flow with laminates prepared with the same processing cycle but with different lots of the same fiber can easily be seen. No final definitive solution was developed for predicting the varying flow response of different fibers and lots. The problem is common with other high-performance resin systems and various fiber reinforcements, and it simply means that, in exacting application, some nominal attention will have to be given to identifying process behavior responses with the specific fiber employed.

3.3.4.4 Thick Laminates

All of the data reported to this point were gathered on relatively thin laminates, i.e., in the 2.3 mm (0.090 inch) thickness range. Thick laminates, more representative of real hardware applications, were fabricated and evaluated. HT-S fiber was selected since this would be the reinforcement employed in fabricating the fan blades in a subsequent phase of the program. These thick laminates were 10.2 cm x 10.2 cm (4 x 4 inches) and in the 1.3 cm (0.5 inch) thickness range.

A thick unidirectional laminate was prepared by imidizing in the tool for 5-1/2 hours at 121°C (250°F); this represented four actual hours at 121°C, discounting the heat-up time. The preform was dropped into a 316°C (600°F) die with a dwell of 60 seconds before pressure application of 6.9 MPa (1000 psi). Target thickness was 1.52 cm and the final actual reading was 1.50 cm. An

examination of the cross section revealed a porous area in the middle of the laminate (see figure 7). It was concluded that the high temperature insertion caused the outer material to cure to a solid mass before the heat reached the center where the partially imidized material was still releasing condensation volatiles. With this in mind, a slower process cycle was evaluated.

The second thick laminate was made up with a ply orientation simulating that of the fan blade demonstration item. This orientation is described below:

Ply No.	Angle in Deg.	Thickness Per Ply	Number of Plies
1	+40	0.254 mm	
2	-40	↓	
3	+40		
4	-40		8
5	+40		
6	-40		
7	+40		
8	-40	↓	
9	+20	0.127 mm	2
10	-20	0.127 mm	
11	0	0.254 mm	
↓	↓	↓	36
46	0	0.254 mm	
47	-20	0.127 mm	2
48	+20	0.127 mm	
49	-40	0.254 mm	
50	+40	↓	
51	-40		
52	+40		8
53	-40		
54	+40		
55	-40	↓	
56	+40	0.254 mm	

This laminate was prepared by imidizing as before, but the part was then put into a 232°C (450°F) die and held at this temperature for 10 minutes under contact pressure before 4.8 MPa (700 psi) was applied and the temperature brought to 316°C at 4.2°C per minute (7.5°F/min.). While minimum flow (less than 1%) was observed, the part was to target size and was determined to be void-free on the basis of sonic C-scan and multiple photomicrographs. As might be expected, because of the specific cross-plied construction, fabrication residual stress cracks were present in the unidirectional core portion; there were 12 easily discernible cracks across the 10.2 cm width. These can easily be seen in figure 8.

3.3.4.5 Postcure

It was determined from data shown in table V that a postcure is required with this matrix if composites are to be evaluated at temperatures representing the materials's maximum. On the previous program (3) conducted with purchased BTDE, it was necessary to use a lengthy cam-controlled oven cycle to achieve the recommended final 343°C temperature without blistering the laminates. With the PMR-15 system using the freshly prepared BTDE, it was found postcure time could be significantly reduced. Multiple laminates of both HM-S and HT-S were postcured successfully by bringing the laminates up to the final temperature over an eight-hour period and then soaking overnight (16 hours) at the final 343°C temperature. Laminate blistering was not observed with this cycle.

In order to determine if this might, in fact, be shortened, a series of panels were subjected to a shock postcure at 343°C (650°F). Four different 10.2 x 10.2 cm (4 inch x 4 inch) laminates, in two different oven runs, were put into a preheated (343°C) oven and held four hours. Only one laminate out of the four blistered in this treatment. The laminates are described in table VII along with the results of the measurements made, including width and weight changes.

Since these trials looked encouraging, an extreme treatment was designed and the three non-blistered laminates described above were further postcured, in two separate oven runs, as follows:

343°C (650°F)	one hour (343°C insertion)
371°C (700°F)	one hour
399°C (750°F)	one hour
427°C (800°F)	four hours

The results of these trials are also described in table VII.

While all three laminates were blistered at the end of this time, laminate 672-46 exhibited only slight effects. Weight and width changes were significant, but it is felt that the conditions were extreme and the tests did demonstrate a markedly reduced sensitivity to temperature rate changes in postcuring obviating the need for an elaborate cam cycle and reflected the behavior of a truly high-temperature performance system.

Since it is probable that systems of this nature will frequently be used in environments that do not demand ultimate performance, additional experiments were conducted. A PMR-15/HM-S laminate was cut into test specimens, without postcure of any kind, and tested at room temperature and 204°C (400°F). The laminate chosen, 672-48, was imidized one hour at 149°C (300°F) and molded by placing the preform into a tool preheated to 316°C (600°F) and held 60 seconds before the application of 6.9 MPa (1000 psi) and the hold at 316°C for one hour. The test results are shown in table VIII; these values are quite good and demonstrate that the PMR-15 system does not require a postcure if less than maximum temperature usage is anticipated.

With the excellent test results obtained at 204°C (400°F) without postcure, it was decided to determine the response at 232°C (450°F). A series of

PMR-15/HT-S laminates were prepared and tested, without postcure, at 232°C. Imidization conditions were varied on these laminates, but the molding technique was that of insertion into a mold at 232°C with a hold of 10 minutes before the application of 6.9 MPa and temperature increase of 316°C. Details of the cycle for each laminate are given in table VI and the resultant mechanical test data are summarized in tables IX and X. The values indicate that the material is fully structural at 232°C without a postcure. Additionally, it can be seen that the effect of postcure on strength at 232°C is minimal, although some minor improvement was observed in room temperature flexural values.

Tables XI and XII list the mechanical properties of two PMR-15/HT-S laminates postcured for 16 hours at 343°C (650°F) before test at 316°C (600°F). In comparing the percent of strength retention number exhibited with those of the laminates tested at 204°C and 232°C, without postcure, it can be seen that strength retention percentages compare well with those of postcured laminates tested at 316°C. It is clear that postcure is not needed unless the material is to be evaluated at its maximum capability.

3.3.4.6 PMR-15 Process Optimization Summary

Since a number of various processing techniques and modifications were discussed, a review of the process work accomplished with the PMR-15 system is given below. Some of the statements are based on incomplete studies, and others concern techniques which may not have immediate application but tend to document special characteristics about the behavior of the system which might have value in special situations.

a) Excessive flow during imidization can be induced from a prepreg stack by very low pressures. A special processing technique based on this fact may be useful.

b) Imidization times and temperatures (either in an oven or in the tool) can be widely varied and have an influence on the resin flow obtained during subsequent molding.

c) Imidizing conditions specified and the flow obtained are, to some degree, dependent upon the characteristics of the fiber reinforcement.

d) Preliminary work has indicated that imidized preforms inserted in the molding tool preheated to 288°C (550°F), and held at this temperature for some time before being brought to 316°C (600°F), exhibited a semi-fluid consistency for approximately 10 minutes. Laminates prepared in this manner displayed a somewhat lower shear strength than composites processed with other cycles. This viscosity behavior might be useful in special applications; e.g., in the case of random molding material, where such a viscosity plateau might provide a long flow period required to fill a complex tool.

e) Mechanical property evaluations of thin laminates demonstrated the equivalent performance of composites prepared by inserting preforms into tools initially preheated to 316°C and 232°C, although the higher insertion temperature method yielded higher flow characteristics. However, the 232°C (450°F) insertion technique came to be

preferred for the following reasons:

1) Less operator risk in working with the lower temperature tool.

2) The 232°C method permits the repositioning of preforms in the tool before the resin softens and begins to stick to the tool.

3) The short dwell times, measured in seconds, that must be employed with the 316°C method demand very rapid response from the equipment and the operator.

4) In thick parts, it was shown that the 316°C technique did not permit the part to come to thermal equilibrium and the accompanying resin solidification lead to non-uniform flow and consolidation patterns.

The 232°C (450°F) molding process, which was adopted as a standard, is described in table XIII. Later work confirmed that this process cycle was fully satisfactory

3.4 Additional Composite Evaluation

The work described in section 3.3.4 characterized the mechanical properties of both HM-S and HT-S unidirectionally reinforced PMR-15 laminates prepared with various processing cycles, with and without postcure, at room temperatures, 204°C (400°F), 232°C (450°F) and 316°C (600°F). The effort described below discusses other characterization investigations.

3.4.1 Isothermal Behavior

In order to compare the isothermal performance of PMR-15/HM-S laminates prepared with fresh BTDE vs. laminates previously fabricated using the same matrix system except with purchased BTDE, a 1000 hour isothermal gravimetric analysis (ITGA) at 316°C (600°F) was run with an air flow of 100 ml/min under the same conditions reported in CR-121275 (3). Two laminates were prepared using the 232°C (450°F) die insertion temperature with a 10 minute dwell period before the application of 6.9 MPa (1000 psi). Portions of these laminates were periodically withdrawn from the exposure oven during the test and tested in flexure and shear at 316°C. The weight loss curve is shown in figure 9 on the same plot with the previously collected data. Excellent agreement was observed, indicating no change in isothermal behavior as a result of the use of the freshly prepared BTDE.

The mechanical test data collected are displayed in table XIV; it is clear that the strength values shown throughout the 1000 hour period demonstrate the excellent strength retention characteristics of the PMR-15 system. In comparing these values with the 316°C data collected on laminates prepared with impure BTDE (see table XV) on previous work (3), it can be seen that the room temperature and short term elevated flexural properties have been significantly improved.

3.4.2 Comparison of PMR-15 and PMR-11 FMW Composites

As was noted previously, a number of experiments were performed to identify processing cycles yielding higher flow with the PMR-15 matrix. While adequate flow was ultimately obtained with the PMR-15, it was felt worthwhile to expend limited effort with the PMR-11 (1100 FMW) system. Prior work (3) had shown higher flow and no loss of ITGA performance with this formulation.

The 1100 FMW material was prepared in the manner described for the 1500 FMW except the ratios of monomeric reactants were altered. The following mole ratios were used:

NE: 2.000
BTDE: 1.257
MDA: 2.257

Processing responses throughout were the same as for the 1500 system, except that the 1100 FMW displayed about four times as much flow for a given process cycle.

A single unidirectional PMR-11/HT-S laminate was tested for mechanical properties at room temperature and 232°C (450°F) in the unpostcured condition. The laminate was processed with a three-hour imidization at 121°C (250°F) and molded with the 10 minute hold at 232°C (450°F) before the application of 6.9 MPa (1000 psi) and temperature increase to 316°C (600°F). This method yielded a 10 w/o flow which resulted in a high fiber fraction (67 v/o). The data collected can be seen in table XVI; even with the high fiber fraction, these represent exceptional strength properties. Also note the retention of 232°C properties of the system without postcure.

A ±10 degree laminate was fabricated with the PMR-11 system and tested in room temperature tensile. The values collected are compared to equivalent laminates of PMR-15 in table XVII. While the average PMR-11 tensile shown is lower than that of the PMR-15, multiple samples should be tested before any judgment is made. This latter statement is made because of the difference shown between PMR-15 laminates 702-4 and 705-16, which varied only in the per-ply thickness of the prepreg. If such a difference (177 MPa) is shown between laminates prepared with only a per ply thickness difference, then it is obvious that the results of a single PMR-11 laminate should not be accepted as complete evidence. The high values observed with the PMR-15 and the very gradual decay shown with increasing angle indicate the ability of the matrix to transmit applied load from fiber to fiber. It is felt that the "toughness" of the matrix is reflected in this performance.

No final conclusions can be drawn on the basis of the work described using the PMR-11 matrix, but the preliminary effort does indicate that the system displays considerable merit. Further work is clearly indicated with the PMR-11 to identify any possible deficiencies and fully define the system so that the higher flow characteristic may be taken advantage of in hardware applications that may require it.

3.5 Fan Blade Fabrication and Characterization

The concluding phase of the program involved the fabrication of hardware items to demonstrate the fabricability and capability of the PMR-15 polyimide system. Selected for the demonstration was a highly complex fan blade developed on contract NAS3-15335. It is the objective of that program to develop and evaluate the aerodynamics of a jet engine fan stage operating at blade tip speeds of 2200 ft/sec (671 m/s) which represents a significant advancement in airfoil and airflow technology. Owing to the high stresses developed by the ultra-high speeds, graphite/polyimide was selected as the material of construction because of its high specific strength and stiffness and high temperature capability. TRW is a subcontractor on this program, charged with the design and build of necessary tooling; the development and implementation of a quality assurance plan; and the fabrication and delivery of a complete wheel-set of blades. Figure 10 shows one of these blades in its finished machined condition; the unusual airfoil configuration can be clearly seen. The blade was an excellent and timely item for demonstrating PMR-15 polyimide resin capability. Four of these blades were fabricated and evaluated on the program.

The only changes introduced include the substitution of the PMR-15/HT-S system and the necessary processing changes required to mold this material. Ply orientation, shapes and number were exactly those previously used on the NAS3-15335 High Tip Speed Blade Program. Additionally, the tooling (both layup and molding) from the NAS3-15335 program was used, as well as the root wedge configuration and material.

3.5.1 Process Preparation

The majority of the basic techniques to accomplish the molding of this complex hardware component had already been developed during the course of this program. Structural requirements of the blade indicated that the HT-S fiber should be used and the PMR-15 formulated molecular weight system was chosen since the most confidence had been gained with this FMW.

Both 0.127 mm and 0.254 mm (5 and 10 mil) prepreg were required and were prepared using the standard techniques described. A critical item in fabrication of this kind is close control of prepreg thickness and resin content. Because the blade is constructed by assembling 77 individual plies, a small variation in molded ply thickness is cumulative and results in a blade that is not to blueprint dimensions (actual blade thickness tolerances are ±1%). To monitor this critical parameter, a "dink" test was used in which a prepreg specimen of known area was used for determining volatile and resin solids and fiber content. Using these figures, an areal density was calculated for the fiber concentration and the values compared to the theoretical optimum which was related to required ply thickness. Both the prepregging techniques and the "dink" test were found to be completely satisfactory for manufacturing and controlling the material limits.

Previous work (3) had been done that indicated that the PMR-15 resin system, when used with an appropriate primer, was completely suitable for the adhesive to be used in the integral molding of the aluminum root wedges.

Therefore, there was no need to identify an auxiliary adhesive and develop suitable fabrication techniques.

The process cycle selected was the standard described in table XIII. As was noted, this cycle is best suited for components of varying cross-section which require different amounts of time to come to thermal equilibrium. The fan blade ranges in thickness from 13.8 mm (0.545 inch) to 0.55 mm (0.022 inch) and a cycle of this type was felt to be a necessity.

The only other specific work required in preparation for the fan blade processing was the fabrication of one special orientation laminate which was an attempt to identify a ply orientation yielding a lower order of residual stress in the composite. Table XVIII gives the specific ply orientation provided by NASA-Lewis personnel. Laminate size was 10.2 cm x 20.3 cm x 0.66 cm (4 inches x 8 inches x 0.260 inch) with a ratio of shell-to-core thickness of 27.4%. The prepreg employed was 40 days old, so, as a safety precaution, the final molding pressure was increased to 13.8 MPa (2000 psi). The standard 232°C (450°F) die insertion mold cycle was used with a two-hour imidization at 121°C (250°F) and a final hold of 1-1/2 hours in the mold at 316°C (600°F).

No axial stress cracks were present after molding as determined by X-ray. The ultrasonic C-scan was clear and multiple polished cross-sections revealed a void-free composite; figure 11 is representative and shows, at 50X magnification, a section taken from the center of the laminate. Table XIX lists the mechanical test data collected at room temperature.

3.5.2 Blade Fabrication

Each of the four fan blades was fabricated in essentially the same manner. The 6061-T6 aluminum wedges were prepared by etching in a standard chromic-sulfuric acid solution for treating aluminum for bonding. All surfaces were then sprayed with a very light coat of BR-34 adhesive primer from Bloomingdale Division of American Cyanamid and dried as recommended. The wedges were then brush coated with a 50 w/o PMR-15 solution and a piece of un-imidized 0.127 mm (5 mil) prepreg laid into the relief machined in the wedges to accept the film adhesive normally used. These prepared wedges were then inserted into the prepreg layups at the appropriate locations shown in Table XX.

Table XX shows the individual ply orientation and ply thicknesses used in each blade. The first three blades, S/N's T-1 through T-3, used the same orientation as shown in the column headed T-2. The T-4 ply orientation, as shown in table XX, was modified. This latter orientation, as provided by the NASA-Lewis Project Manager was chosen to reduce residual stresses in the molded part and was based on the good results of the trial laminate discussed in the previous section dealing with preparation for blade molding.

The blade layups were accomplished in two halves on special layup tools. The two halves of the laid-up blade stacks were mated and sandwiched between TFE coated glass cloth with four plies of silicone treated glass cloth as bleeder on either side of the completed layup. These sandwiches were placed in the molding tool at room temperature and contact pressure applied to the layup. The die punch was then raised 5 mm (0.200 inch) to allow for some

expansion of the layup during the imidization process and the temperature brought to 121°C (250°F) over a one-hour period. This was done in small increments to prevent the evolution of volatile materials from occurring too rapidly and distorting the prepreg layup. The die was held at 121°C for 4-1/2 hours (Blade S/N T-1) or 2 hours (T-2, T-3 and T-4), and the die force-cooled to room temperature. At this point, the imidized parts were removed from the tool and inspected for integrity and any possible fiber distortion.

The parts were easily handled without fear of disintegration, and no significant distortion of surface ply orientation was observed. The imidized parts were dry-fitted back into the cold die to check ease of installation (no stock removal was required) and put to one side. The die was then heated to 232°C and brought to thermal equilibrium. At this point, the root end-rail of the die was removed so that the parts could be placed in the tool with ease. The parts were installed and the end-rail re-secured and contact pressure applied to the part. At the end of 10 minutes, pressure was increased to 5.5 MPa (800 psi) and the die brought up to 316°C (600°F) over a 20 minute period. The part was held at this temperature for 1-1/2 hours (T-1, T-2 and T-4) or 3 hours (T-3) and the cooling process started. The die was cooled by blowing air from a fan over the die until the punch and die were at 260°C (500°F) and the pressure reduced to 1.9 MPa (270 psi) and fan cooling continued until the punch and die thermocouples indicated 204°C (400°F). The pressure was then reduced to contact and water cooling used to cool to room temperature.

3.5.3 Blade Characterization

The parts exhibited an excellent surface appearance after molding and seemed fully consolidated. Resin expulsion observed around the die was negligible. Root bond of the 6061-T6 wedges on T-1, T-2 and T-4 seemed good for the most part, although some minor lifting at two diagonally opposed corners was observed; this was not considered significant since this portion would ordinarily be removed in finish machining. Five spot checks for dimensional conformance were made on the as-molded blades. These include three points at the tip and two points on the transition from root to airfoil. The tip sections measured represent an area machined off the blade in final processing. Table XXI shows a comparison of these five points for each blade vs. the blueprint dimension.

Table XXII gives the weights of the four blades after the various processing steps. The significant item to note is the close correlation of the weights at each step of the process among the three parts molded.

All four blades were ultrasonically inspected by the prime contractor; schematics showing the defect areas identified in S/N's T-1 through T-3 are illustrated in figures 12 through 14. No defect map is shown for T-4 since the ultrasonic examination did not reveal any indications. The large defect area discovered in T-3 is commented on below. No final explanation of the sonic defects found in T-1 and T-2 is available. Before the ply orientation change in T-4, it was hypothesized that the sonic indications, since they fell in about the same area, were possibly connected to a ply-shape problem or might have been the result of inadequate resin flow. The low residual stress

ply orientation employed in T-4 resulted in a sonically "clean" blade. This piece of information lead to a third hypothesis, i.e., that the sonic indications might have been the result of internal residual stresses causing localized delamination. Two other bits of information seem to lend credence to this theory. The first is that the sonic indications observed were geographically related to a sharp, localized change in the contour of the airfoil; this sort of extreme configuration change can be presumed to be the location of a high residual stress concentration. The second piece of information tends to minimize the value of the two alternate hypotheses. The prime contractor did an extensive microscopic study of S/N T-2 and found no evidence of voids in the area of the sonic indications. This fact would eliminate possibility of inadequate resin flow or inadequate consolidation due to ply shape deficiencies. Without further experimentation then, it is felt that the sonic indications result from the internal residual stresses present in a complex piece of hardware made up with multiple ply shapes and fiber orientations.

Radiographic examination of the blades after molding confirmed the efficacy of the low residual stress ply orientation; S/N T-4 showed no axial stress cracks. The presence of this type of crack in the other blades was quite clearly shown in the X-rays. The number of cracks observed is summarized below:

S/N	Number of Cracks
T-1	6
T-2	5
T-3	9
T-4	0

The resistance to stress cracking of the PMR-15 matrix can be best understood when compared to the matrix previously employed. This latter system yielded about 20 axial cracks when the ply orientation used in S/N's T-1 through T-3 was employed.

S/N T-3 exhibited less than acceptable sonic and dimensional quality although similar procedures were followed for each blade. While the blade was not sectioned, a hypothesis was formulated to account for the inferior quality. When T-3 was removed from the die, the two side rails at the root end were observed to display a deposit of aluminum. An examination of the blade root showed two of the wedges were buckled and exhibited separation from the composite sections interleaved between the wedges. The wedges used were originally inspected on a statistical basis and it seems possible that a long set of wedges was selected, and in heating to 316°C (600°F), these expanded to a length greater than could be accommodated by the steel die, resulting in an interference. It is thought that this interference could have prevented the punch from closing completely, thus permitting the airfoil section to cure with less than the planned pressure. If this were true, the possibility for voids or a weakened ply bond can readily be seen, leading to identifiable sonic defects.

As a preventative measure, the wedges for S/N T-4 were reduced in length. In this way, the possibility of interference between die and wedges, the supposed cause of sonic defects in S/N T-3, was eliminated.

Serial number T-4, with the low stress ply orientation, was subjected to natural frequency tests by the prime contractor. The results are summarized below:

First Bending Mode	269 Hertz
Second Bending Mode	997 Hertz
First Torsional Mode	808 Hertz

Spin-test/data on two of the PMR-15 fan blades were collected on contract NAS3-15335. Blade S/N T-1 was spun to 100% of design speed (15,200 rpm, 2200 ft/sec) whereupon catastrophic failure occurred. A post-test analysis revealed anomalies in the test data and rig performance making an accurate determination of the cause of failure impossible. Blade S/N T-2 was similarly evaluated but with complete success. Evaluation procedures included 50 cycles in low cycle fatigue (spun to 100% speed); 10^7 cycles in high cycle fatigue (vibratary loading in first bending mode at 10 ksi load at maximum stress point); and finally, an additional 10 cycles in low cycle fatigue. The blade remained intact through all of this testing but did reveal considerable internal delamination when it was cross-sectioned and examined microscopically.

While certain spin test conditions and equipment parameters have yet to be finally resolved, it is felt that the results of the blade testing to date indicate that the PMR-15/HT-S system is capable of sustaining the load levels imposed by the current design goals.

4.0 PROGRAM CONCLUSIONS

The polymerization of monomeric reactant (PMR) approach to the chemistry and processing of advanced resin matrices was found to be valuable, significant and worthy of continued attention in both development and commercial applications. Specific conclusions on such items as processing details and material properties are presented in the body of the text. The conclusions given below represent those major statements that summarize the overall findings of the program. Since two matrices were studied, the conclusions for each are shown separately.

Polyphenylquinoxaline

1. The PMR approach to the preparation of polyphenylquinoxaline (PPQ) prepreg resolved many of the classic problems associated with this type of polymer. Monomer solution mixing was easily achieved at room temperature in a safe solvent, 1-methyl-2-pyrrolidinone, at the relatively high concentrations of 30-35 w/o. Application of the low viscosity solution to the fiber yielded an even distribution and the prepreg was easily devolatilized to yield a material with excellent drape and tack. Moldability of the prepreg was not affected by room temperature storage up to three weeks.

2. Essentially void-free PPQ composites were fabricated in a straightforward manner, but limited flow was obtained and the process utilized led to the autoignition of the residual solvent evolved during the first few seconds of process time.

3. The room temperature mechanical properties of the PPQ/HM-S laminates were typical for composites of this reinforcement. However, 316°C performance before postcure was found to be inadequate, due to thermoplasticity, indicating that further work is required.

Polyimide

1. The PMR approach to the fabrication of thermo-oxidatively stable polyimide laminates was found to be a practical one which provided many advantages. Both resin solution and prepreg were determined to be unchanged within the limits of normal good practice. Prepregging, layup, solvent removal and imidization were found to be safe and straightforward.

2. Molding of void-free composites was achieved by a number of different process cycles and the preferred cycle eliminated operator judgment factors and displayed extremely wide processing control limits. Modification of the stoichiometry provided matrices exhibiting a range of flow characteristics from adequate to excessive with no loss of property performance.

3. In direct comparison with previous work, it was determined that prior efforts had been performed with purchased ester-acid which interfered with the achievement of void-free composites. The use of freshly esterified material completely eliminated any trace of this problem.

4. Isothermal gravimetric analysis at 316°C (600°F) confirmed the previously reported excellent thermo-oxidative performance, indicating a long-term service life in the range of 288°C to 316°C.

5. The fabrication of four large fan blades with an extremely complex configuration revealed no process problems and resulted in void-free components suitable for service testing. The success achieved, with the limited number of trials available for experimentation, clearly indicates that the PMR polyimide system is ready for immediate commercial application.

5.0 RECOMMENDATIONS

The multiple advantages of the polymerization of monomeric reactants concept were amply demonstrated in the course of the experimental work described in the body of the text. In the case of the polyphenylquinoxaline matrix, further development work is required. In the area of processing, it is suggested that additional work be performed to identify a fabrication cycle that provides more resin flow and eliminates the problem of autoignition of the carrier solvent. The limited composite evaluation conducted indicates that elevated temperature performance requires further effort which might fall into the category of thermal post-treatments or in chemistry modification to reduce residual thermoplasticity in the molded composite. Presuming the achievement of this objective, then additional characterization of composite systems would be required.

On the basis of the data presented in this document, the conclusion must be drawn that the PMR polyimide matrix system is ready now for commercial application. It is suggested that additional areas of interest lie in further characterization of potential process advantages of the lower formulated molecular weight materials. Other suggested investigations include a comparison of a range of formulated molecular weight materials in such areas, for example, as cryogenics, fluid resistance, fracture toughness and wear. Additional fabrication processes should be investigated; e.g., the compression and transfer molding of chopped random moldings with various fibrous reinforcements and the determination of the feasibility of autoclave processing.

TABLE I

HM-S/POLYPHENYLQUINOXALINE LAMINATE MECHANICAL PROPERTIES BEFORE POSTCURE

Property	Laminate No.	At 22°C (72°F) SI Units (U.S.)	At 316°C (600°F) SI Units (U.S.)
Flexural Strength	669-31	1249 MPa (181.2 ksi)	-
↓	669-53	1180 MPa (171.1 ksi)	105 MPa (15.2 ksi)
↓	669-81	-	80 MPa (11.5 ksi)
Flexural Modulus	669-31	161 GPa (23.3 msi)	-
↓	669-53	161 GPa (23.4 msi)	-
↓	669-81	-	-
Short Beam Shear Strength	669-31	68 MPa (9800 psi)	-
↓	669-53	71 MPa (10,300 psi)	-

NOTE: All values represent average of three specimens.

TABLE II

WEIGHT PERCENT RESIN FLOW OBTAINED IN MOLDING PMR-15/HM-S LAMINATES WITH VARIOUS IMIDIZATION/MOLD CONDITIONS

121°C (250°F) Oven Imidize

Imidization Time, hrs	Dwell Time Before Pressure Application 30 seconds	60 seconds
1	7.1 w/o	1.8 w/o
2	6.2 w/o	<1.0 w/o
3	6.8 w/o	<1.0 w/o

149°C (300°F) Oven Imidize

Imidization Time, hrs	Dwell Time Before Pressure Application 30 seconds	60 seconds
1/2	3.3 w/o	<1.0 w/o
1	1.5 w/o	<1.0 w/o
2	2.1 w/o	<1.0 w/o

NOTE: 316°C (600°F) and 6.9 MPa (1000 psi) used for all conditions.

TABLE III

FLOW AND SONIC RESULTS OF PMR-15/HM-S LAMINATES MOLDED WITH VARIOUS DWELL TIMES/INSERTION TEMPERATURES BEFORE PRESSURE APPLICATION

Insertion Temp., °C	Dwell Time, Minutes: 1/2	1	1-1/2	2	3	5	10	Insertion Temp., °F
316	S = 0 F = 6							600
288	S = 0 F = 9	S = 0 F = 3	S = 0 F = 4					550
260		S = 22 F = 2		S = 19 F = 2	S = 0 F = 2			500
232		S = 100 F = 1			S = 10 F = 1		S = 9 F = 1	450
204		S = 100 F = 1				S = 37 F = 1		400

NOTES: a) S = sonic defect area in %.
F = flow w/o based on total composite weight.
b) All laminates oven imidized 3 hours at 121°C (250°F).
c) Final molding temperature 316°C (600°F) at 6.9 MPa (1000 psi) for 1 hour.

TABLE IV

PROPERTY COMPARISON OF PMR-15/HM-S LAMINATES WITH TWO ALTERNATE MOLDING CYCLES

	22°C (72°F)	316°C (600°F)	% at Room Temperature Retention
Short Beam Shear			
Lam 672-73	38.6 MPa (5.6 ksi)	33.0 MPa (4.8 ksi)	86
Lam 672-74	39.9 MPa (5.8 ksi)	34.4 MPa (5.0 ksi)	86
Flexural Strength			
Lam 672-73	1243 MPa (180.3 ksi)	997 MPa (144.7 ksi)	80
Lam 672-74	1238 MPa (179.7 ksi)	907 MPa (131.6 ksi)	73
Flexural Modulus			
Lam 672-73	169 GPa (24.6 Msi)	166 GPa (24.1 Msi)	98
Lam 672-74	162 GPa (23.6 Msi)	160 GPa (23.3 Msi)	99

NOTE: a) Each value shown represents the average of three specimens.

b) Both laminates were molded exactly alike except that 672-73 was given a one hour hold at 288°C before being raised to 316°C.

TABLE V

MECHANICAL TEST COMPARISON OF TWO DIFFERENT CURE CYCLES OF PMR-15/HM-S LAMINATES

		Insert 232°C (450°F) 10 Min Dwell		Insert 316°C (600°F) 30 Sec Dwell	
		No Postcure	Postcure	No Postcure	Postcure
Room Temp. Test	SBS	Lam. 672-5 9.3 9.1 8.1 Avg 8.8 ksi 60.7 MPa		Lam. 672-44 8.7 8.7 8.2 Avg 8.5 ksi 58.6 MPa	
	Flex	Lam. 672-5 Stg. / Mod. 183.4 / 24.9 203.9 / 26.5 200.8 / 25.3 Avg 196.0 ksi / 25.5 msi 1351 MPa / 176 GPa		Lam. 672-44 Stg. / Mod. 174.0 / 27.1 189.6 / 26.9 184.0 / 26.7 Avg 182.5 ksi / 26.9 msi 1258 MPa / 185 GPa	
316°C (600°F) Test	SBS		Lam. 672-5 6.6 6.4 6.8 Avg 6.6 ksi 45.5 MPa	Lam. 672-56 3.0 3.6 3.0 Avg 3.2 ksi 22.1 MPa	Lam. 672-36 6.3 6.6 6.4 Avg 6.4 ksi 44.1 MPa
	Flex		Lam. 672-5 Stg. / Mod. 109.3 / 21.5 145.0 / 22.2 147.6 / 22.6 Avg 133.9 ksi / 22.1 msi 923 MPa / 152 GPa	Lam. 672-56 Stg. / Mod. 56.9 / 11.7 68.2 / 15.1 84.8 / 19.0 Avg 69.9 ksi / 15.2 msi 482 MPa / 105 GPa	Lam. 672-36 Stg. / Mod. 164.6 / 25.2 159.1 / 25.3 156.1 / 25.1 Avg 159.9 ksi / 25.2 msi 1102 MPa / 174 GPa
Resin Solids, w/o		33.6	33.6	28.4/30.3	27.9
Specific Gravity		1.63	1.63	1.67/1.65	1.66
Fiber Vol., v/o		57.8	57.8	64.2/61.5	64.3
Void Content, v/o		0.7	0.7	0.0/0.6	0.6

NOTES: 1) All tests run in triplicate.
2) Postcure 16 hours at 343°C.
3) Oven Imidization: 672-5: 204°C/1 hr 672-44: 121°C/3 hr
672-36: 121°C/1 hr 672-56: 121°C/2 hr
4) Final mold temperature: 316°C for one hour at 6.9 MPa
5) All sonic C-scans clear.

TABLE VI

PMR-15/HT-S LAMINATE PROCESSING SUMMARY

Laminate No.	Imidization Temp. °C	Imidization Temp. °F	Imidization Time Hrs	Insertion Temp. °C	Insertion Temp. °F	Dwell Time	Flow w/o	Quality	Prepreg No.	Fiber Lot/Spool	Notes
672-99	121	250	3	316	600	45 sec	8.2	OK, high mech. values	672-97	9-2/2A-1	
672-100	121	250	3	288	550	30 sec + 15 min	10.2	Sonic poor	672-97		
701-1	121	250	3 (in tool)	288	550	30 sec + 15 min	12.0	Sonic poor	672-97		
701-2	121 204	250 400	3 1	316	600	30 sec	6.8	OK, high mech. values	672-97		
701-9	121	250	3	288	550	30 sec + 15 min	14.0	Sonic poor	672-97		
701-12	121	250	4 (in tool)	316	600	60 sec	8.7	Sonic good	672-97		
701-17	204	400	1	316	600	90 sec	11.0	Sonic fair	701-5	9-2/2A-1	
701-20	204	400	2	288	550	90 sec	<1	Sonic good	701-19	9-2/91A-3	
701-21	204	400	2	316	600	60 sec	<1	Sonic good	701-19	9-2/91A-3	
701-29	121	250	3	232	450	10 min	4.4	Sonic good	701-27	9-2/91A3	
701-30	121	250	24	316	600	30 sec	9.4	Sonic good	701-27	9-2/91A3	
701-44	204	400	2	232	450	10 min	0	- - - - -	701-33	27-1/-	0.25 mm, 0/90, 3.4 MPa
701-47	204	400	2		450	10 min	<1	Sonic good	701-37		0.12 mm, 0/90, 3.4 MPa
701-58	121 204	250 400	1/2 1		450	10 min	<1	Surface OK	701-33		
701-66	121	250	3		450	10 min	1.5	Sonic good	701-33		
701-68	121	250	2		450	10 min	2.7	Sonic good	701-33		
701-69	121	250	1		450	10 min	3.0	Sonic good	701-33		
701-86	121	250	3	316	600	60 sec	4.2	- - - -	701-79	27-1/-	

TABLE VII

POSTCURE RESULTS ON UNIDIRECTIONAL PMR-15/HM-S COMPOSITES

	First Trial		Second Trial	
Laminate No.	672-35	672-46	672-26	672-37
Process				
Imidization	2 hr/163°C	3 hr/121°C	2 hr/204°C	2 hr/121°C
Mold Insertion	232°C/10 min	316°C/60 sec	232°C/10 min	316°C/60 sec
Cure	316°C/1 hr	316°C/1 hr	316°C/1 hr	316°C/1 hr
343°C Postcure (650°F)				
Weight Loss, w/o	0.4	0.5	0.6	0.6
Width Change, %	-0.2	-0.2	-0.3	-0.3
Blistered	No	No	No	No
Postcure to 427°C (800°F)				
Additional Weight Loss, w/o	2.2	2.4	-	-
Additional Width Change, %	-1.4	-2.0	-	-
Blistered	Yes	Yes, slight	Yes	-

NOTE: Laminate size 10.2 cm x 10.2 cm x 2.3 mm.

TABLE VIII

ROOM TEMPERATURE AND 204°C MECHANICAL TEST RESULTS OF A PMR-15/HM-S LAMINATE WITHOUT POSTCURE

	22°C (72°F)	204°C (400°F)	% of Room Temperature Retention
Flexural Strength	1210 MPa (175.6 ksi)	1070 MPa (155.2 ksi)	88
Flexural Modulus	163 GPa (23.7 msi)	158 GPa (23.0 msi)	97
Short Beam Shear Strength	66 MPa (9.6 ksi)	53 MPa (7.7 ksi)	80

NOTE: All values shown represent an average of three specimens.

TABLE IX

ELEVATED TEMPERATURE STRENGTH RETENTION OF NON-POSTCURED PMR-15/HT-S LAMINATES

Laminate No.		Test Temperature 22°C (72°F)	Test Temperature 232°C (450°F)	% of Room Temperature Retention
701-68				
Short Beam Shear Strength,	MPa	108	58	54
	Ksi	15.7	8.4	
Flexural Strength,	MPa	1604	1154	72
	Ksi	232.6	167.4	
Flexural Modulus,	GPa	117	112	96
	Msi	16.9	16.2	
701-69				
Short Beam Shear Strength,	MPa	109	63	58
	Ksi	15.8	9.2	
Flexural Strength,	MPa	1680	1298	77
	Ksi	243.6	188.2	
Flexural Modulus,	GPa	130	113	87
	Msi	18.8	16.4	
701-86				
Short Beam Shear Strength,	MPa	121	65	54
	Ksi	17.5	9.4	
Flexural Strength,	MPa	1862	1474	79
	Ksi	270.0	213.8	
Flexural Modulus,	GPa	128	125	97
	Msi	18.6	18.1	

NOTE: Values shown are the averages of 2 to 5 specimens per condition.

TABLE X

COMPARISON OF ELEVATED TEMPERATURE STRENGTH
OF PMR-15/HT-S LAMINATES BEFORE AND AFTER POSTCURE

Laminate No.		Tested at 22°C (72°F) Non-Postcured	Tested at 22°C (72°F) Postcured	Tested at 232°C (450°F) Non-Postcured	Tested at 232°C (450°F) Postcured	% RT Retention (Postcured: Non-Postcured)
701-29						
Short Beam Shear Strength,	MPa	128	119	-	75	59
	Ksi	18.7	17.3		10.9	
Flexural Strength,	MPa	1548	1735	-	-	-
	Ksi	224.5	251.7			
Flexural Modulus,	GPa	125	130	-	-	-
	Msi	18.1	18.8			
701-58						
Short Beam Shear Strength,	MPa	115	-	57	66	57
	Ksi	16.7		8.2	9.6	
Flexural Strength,	MPa	1552	-	1182	1205	78
	Ksi	225.1		171.5	174.8	
Flexural Modulus,	GPa	108	-	108	110	100
	Msi	15.6		15.6	16.0	

NOTE: Values shown are the averages of 2 to 5 specimens per condition.

TABLE XI

ROOM TEMPERATURE AND 316°C MECHANICAL PROPERTIES OF UNIDIRECTIONAL PMR-15/HT-S LAMINATE

	22°C (72°F)		316°C (600°F)		% RT Retention
Short Beam Shear Strength	124.1	18.0	62.7	9.1	
	118.5	17.2	63.4	9.2	
	146.1	21.2	62.7	9.1	
Avg.	131.6 MPa	19.1 ksi	62.7 MPa	9.1 ksi	48
Flexural Strength	1720	249.5	1453	210.8	
	1636	237.3	1310	190.1	
	1711	248.3	1497	217.2	
Avg.	1689 MPa	245.0 ksi	1420 MPa	206.0 ksi	84
Flexural Modulus	136	19.8	128	18.7	
	135	19.7	127	18.5	
	136	19.8	133	19.3	
Avg.	136 GPa	19.8 msi	129 GPa	18.8 msi	95

Imidization: 3 hrs at 121°C (250°F)
Mold Cycle: 45 sec dwell at 316°C, 6.9 MPa, one hour at 316°C (600°F)
Postcure: 16 hrs at 343°C (650°F)
Flow: 8 w/o
V_f: 64.0 v/o
Lam. No.: 672-99

TABLE XII

ROOM TEMPERATURE AND 316°C MECHANICAL PROPERTIES OF UNIDIRECTIONAL PMR-15/HT-S LAMINATE

	22°C (72°F)		316°C (600°F)		% RT Retention
Short Beam Shear Strength	117.9	17.1	56.5	8.1	
	111.7	16.2	59.3	8.6	
	119.2	17.3	57.9	8.4	
Avg.	116.5 MPa	16.9 ksi	57.9 MPa	8.4 ksi	50
Flexural Strength	1979	287.0	1616	234.4	
	1935	280.7	1554	225.4	
	2010	291.5	1473	213.6	
Avg.	1975 MPa	286.4 ksi	1548 MPa	224.5 ksi	78
Flexural Modulus	138	20.0	137	19.8	
	139	20.1	134	19.5	
	138	20.0	136	19.7	
Avg.	138 GPa	20.0 msi	136 GPa	19.7 msi	99

Imidization: 3 hrs at 121°C (250°F) plus 1 hr at 204°C (400°F)
Mold Cycle: 30 sec dwell at 316°C, 6.9 MPa, one hour at 316°C (600°F)
Postcure: 16 hrs at 343°C (650°F)
Flow: 7 w/o
Lam. No.: 701-2

TABLE XIII

PREFERRED PMR-15 MOLDING PROCESS

1. Imidize in the tool or in an air-circulating oven at temperatures ranging from 121°C (250°F) to 204°C (400°F) for times from one to three hours depending upon flow required, resin solids content, and fiber type.

2. Place preform in a die preheated to 232°C (450°F) and apply contact pressure.

3. Hold at this temperature and pressure for 10 minutes and then apply 3.4 to 6.9 MPa (500 to 1000 psi) and raise the temperature to 316°C (600°F) at a rate of 4.2°C/minute (7.5°F/minute).

4. Hold at 316°C for one hour.

5. Cool to 260°C (500°F) and reduce pressure by half.

6. Continue to cool to 204°C (400°F), reduce to contact pressure and introduce cooling water to press platens.

7. Remove part at room temperature.

8. Postcure for 12 to 16 hours at 343°C (650°F) if the part is to be used at the maximum capability of the material.

TABLE XIV

ITGA MECHANICAL TEST DATA OF PMR-15/HM-S COMPOSITES USING FRESHLY PREPARED BTDE

Exposure Time hrs	Exposure & Test Temperature °C	°F	Flexure Strength MPa	ksi	Flexure Modulus GPa	Msi	Short Beam Strength MPa	ksi
-	RT	RT	1296	187.9	167	24.2	66.9	9.7
0.1	316	600	1111	161.2	158	22.9	46.9	6.8
400	↓	↓	868	125.9	152	22.1	40.0	5.8
800			738	107.0	152	22.1	42.1	6.1
1000			654	94.9	142	20.6	33.1	4.8

NOTE: All values represent the average of three specimens.

TABLE XV

ITGA MECHANICAL TEST DATA SUMMARY OF HM-S/PMR-15 COMPOSITES

Exposure Time hrs	Exposure & Test Temperature °C	°F	Flexure Strength MPa	ksi	Flexure Modulus GPa	Msi	Short Beam Shear Strength MPa	ksi
-	22	72	871.2	126.4	163	23.6	84.0	12.2
0.1	288	550	1005.9	145.9	163	23.6	45.5	6.6
200	↓	↓	941.1	136.5	178	25.8	55.6	8.1
500	↓	↓	959.8	139.2	162	23.5	51.7	7.5
1000	↓	↓	999.6	145.0	164	23.7	55.2	8.0
0.1	316	600	959.8	119.7	156	22.6	50.3	7.3
200	↓	↓	923.5	133.9	163	23.6	46.2	6.7
400	↓	↓	853.3	123.8	159	23.1	47.4	6.9
600	↓	↓	896.9	130.1	155	22.5	48.0	7.0
800	↓	↓	767.0	111.2	150	21.7	45.1	6.5
0.1	343	650	715.3	103.7	135	19.6	32.7	4.7
10	↓	↓	884.2	128.2	151	22.0	37.9	5.5
50	↓	↓	754.8	109.5	157	22.8	47.6	6.9

NOTE: a) Values represent average of five specimens.

b) These data are from reference 3 (CR-121275) and were collected on laminates prepared using purchased BTDE.

TABLE XVI

PMR-11/HT-S ROOM AND ELEVATED TEMPERATURE MECHANICAL TEST VALUES

		22°C (72°F)	232°C (450°F)	% Retention
Flexural Strength,	MPa	2177	1844	85
	Ksi	315.8	267.4	
Flexural Modulus,	GPa	138	135	98
	Msi	20.0	19.6	
Short Beam Shear Strength,	MPa	123	67	54
	Ksi	17.8	9.7	

NOTES: a) Laminate not postcured.

b) Values represent average of three specimens.

c) Fiber fraction = 67 v/o.

d) Prepared with the 232°C (450°F) die insertion method with a 3 hour imidize at 121°C (250°F).

TABLE XVII

CROSS-PLY TENSILE STRENGTH OF HT-S LAMINATES WITH PMR-15 AND PMR-11 MATRICES

Material	Laminate No.	Ply Orientation	Ply Thickness mm	Ply Thickness mils	Specimen Width mm	Specimen Width inches	Average Tensile Strength MPa	Average Tensile Strength Ksi
PMR-15/HT-S	702-3	0°	0.254	10	6.35	0.250	1246	180.7
↓	702-5	$\pm 5^{\circ}$	0.127	5	19.05	0.750	1273	184.6
↓	702-4	$\pm 10^{\circ}$	0.127	5	19.05	0.750	1074	155.8
↓	705-16	$\pm 10^{\circ}$	0.254	10	15.24	0.600	897	130.1
PMR-11/HT-S	705-17	$\pm 10^{\circ}$	0.254	10	15.24	0.600	823	119.3

NOTE: All values represent the average of five or more specimens.

TABLE XVIII

PLY ORIENTATION OF PMR-15/HT-S LOW RESIDUAL STRESS PANEL

Ply No.	Orientation, Degrees	Ply Thickness, mm
1	+30	0.127
2	-30	
3	+30	
4	90	
5	-30	
6	+30	
7	-30	
8	-10	0.254
9	0	
10	+10	
11	0	
12	-10	
13	0	
14	+10	
15	0	0.127
16	-10	
17	0	
18	+10	
19	0	Axis of Symmetry
20	+10	0.127
⋮		
37		

TABLE XIX

ROOM TEMPERATURE MECHANICAL PROPERTIES

OF PMR-15/HT-S LOW STRESS PANEL

		MPa	Psi		GPa	Msi
0° Flexure Strength		1033	149,800	Modulus	77	11.1
S/D = 25:1		1084	157,200		77	11.1
		911	132,100		75	10.9
	Avg	1009	146,400		76	11.0
90° Flexure Strength		192	27,900	Modulus	25	3.6
S/D = 12:1						
0° Short Beam Shear		87	12,600			
S/D = 4:1		85	12,400			
		83	12,100			
	Avg	85	12,400			
90° Short Beam Shear		23	3,300			
S/D = 4:1		24	3,500			
		20	2,900			
	Avg	22	3,200			

TABLE XX

HIGH SPEED BLADE LAMINATION LAY-UP SEQUENCE

(FACING PREFORM TOOLS - CLOCKWISE ANGLES ARE POSITIVE)

Convex Blade Half				Concave Blade Half			
	Orientation				Orientation		
Ply No.	T-2	T-4	Prepreg Thickness	Ply No.	T-2	T-4	Prepreg Thickness
1	-75	-75	0.127 mm	75	+75	+75	0.127 mm
2	+75	+75		74	-75	-75	
3	-40	-30		73	+40	+30	
4	+40	+30		72	-40	-30	
5	-40	-30		71	+40	+30	
6	+40	+30		70	-40	-30	
7	-40	-30		69	+40	+30	
8	+40	+30		68	-40	-30	
9	-40	-30		67	+40	+30	
10	+40	+30		66	-40	-30	
11	-40	-30		65	+40	+30	
12	+40	+30		64	-40	-30	
13	-40	-30		63	+40	+30	
14	+40	+30		62	-40	-30	
15	-40	-30		61	+40	+30	
16	+40	+30		60	-40	-30	
17	-40	-30		59	+40	+30	
18	+40	+30	Wedge	58	-40	-30	Wedge
19 a	-20	-30		57 a	+20	+30	
19 b	+20	+30	0.127 mm	57 b	-20	-30	0.127 mm
20	0	+10	0.254 mm	56	0	-10	0.254 mm
21		0		55		0	
22		-10		54		+10	
23		0		53		0	
24		+10		52		-10	
25		0	Wedge	51		0	Wedge
26		-10		50		+10	
27		0		49		0	
28		+10		48		-10	
29		0		47		0	
30		-10		46		+10	
31		0		45		0	
32		+10	Wedge	44		-10	Wedge
33		0		43		0	
34		-10		42		+10	
35		0		41		0	
36		+10		40		-10	
37		0		39		0	0.254 mm
				38	0	0	0.127 mm

TABLE XXI

AS-MOLDED PMR-15/HT-S HIGH TIP SPEED BLADE DIMENSIONS IN MILLIMETERS

Location	B/P Nominal mm	B/P Tolerance mm	T-1 Actual mm	T-1 Deviation from Limit mm	T-2 Actual mm	T-2 Deviation from Limit mm	T-3 Actual mm	T-3 Deviation from Limit mm	T-4 Actual mm	T-4 Deviation from Limit mm
Tip - Leading Edge	0.864	±0.127	1.09	+0.102	1.02	+0.025	1.50	+0.508	-	-
Tip - Maximum	10.1		10.1	-0-	9.96	-0.025	10.2	-0-	9.52	-0.584
Tip - Trailing Edge	1.40		1.42	-0-	1.42	-0-	1.09	-0.178	0.940	-0.457
Root - Leading Edge	13.8		14.1	+0.127	14.1	+0.152	14.5	+0.508	13.7	-0.025
Root - Trailing Edge	13.8		14.0	+0.076	14.1	+0.127	14.4	+0.406	13.6	-0.102

AS-MOLDED PMR-15/HT-S HIGH TIP SPEED BLADE DIMENSIONS IN INCHES

Location	B/P Nominal Inches	B/P Tolerance Inches	T-1 Actual Inches	T-1 Deviation from Limit Inches	T-2 Actual Inches	T-2 Deviation from Limit Inches	T-3 Actual Inches	T-3 Deviation from Limit Inches	T-4 Actual Inches	T-4 Deviation from Limit Inches
Tip - Leading Edge	0.034	±0.005	0.043	+0.004	0.040	+0.001	0.059	+0.020	-	-
Tip - Maximum	0.398		0.397	-0-	0.392	-0.001	0.402	-0-	0.375	-0.023
Tip - Trailing Edge	0.055		0.056	-0-	0.056	-0-	0.043	0.007	0.037	-0.018
Root - Leading Edge	0.545		0.555	+0.005	0.556	+0.006	0.570	+0.020	0.539	-0.001
Root - Trailing Edge	0.545		0.553	+0.003	0.555	+0.005	0.566	+0.016	0.536	-0.004

TABLE XXII

WEIGHT IN GRAMS OF PMR-15/HT-S HIGH TIP SPEED BLADES DURING PROCESSING

Condition	T-1	T-2	T-3	T-4
Weight of Bare Wedge Set	278	277	275	276
Weight of Blade Lay-up Prior to Imidizing	1058	1056	1060	1020
Weight of Blade Lay-Up After Imidizing	998	995	1000	958
Weight of Flash-Free Blade After Molding	987	984	987	947
Weight of Blade After Molding Less Weight of Wedges	709	707	712	671

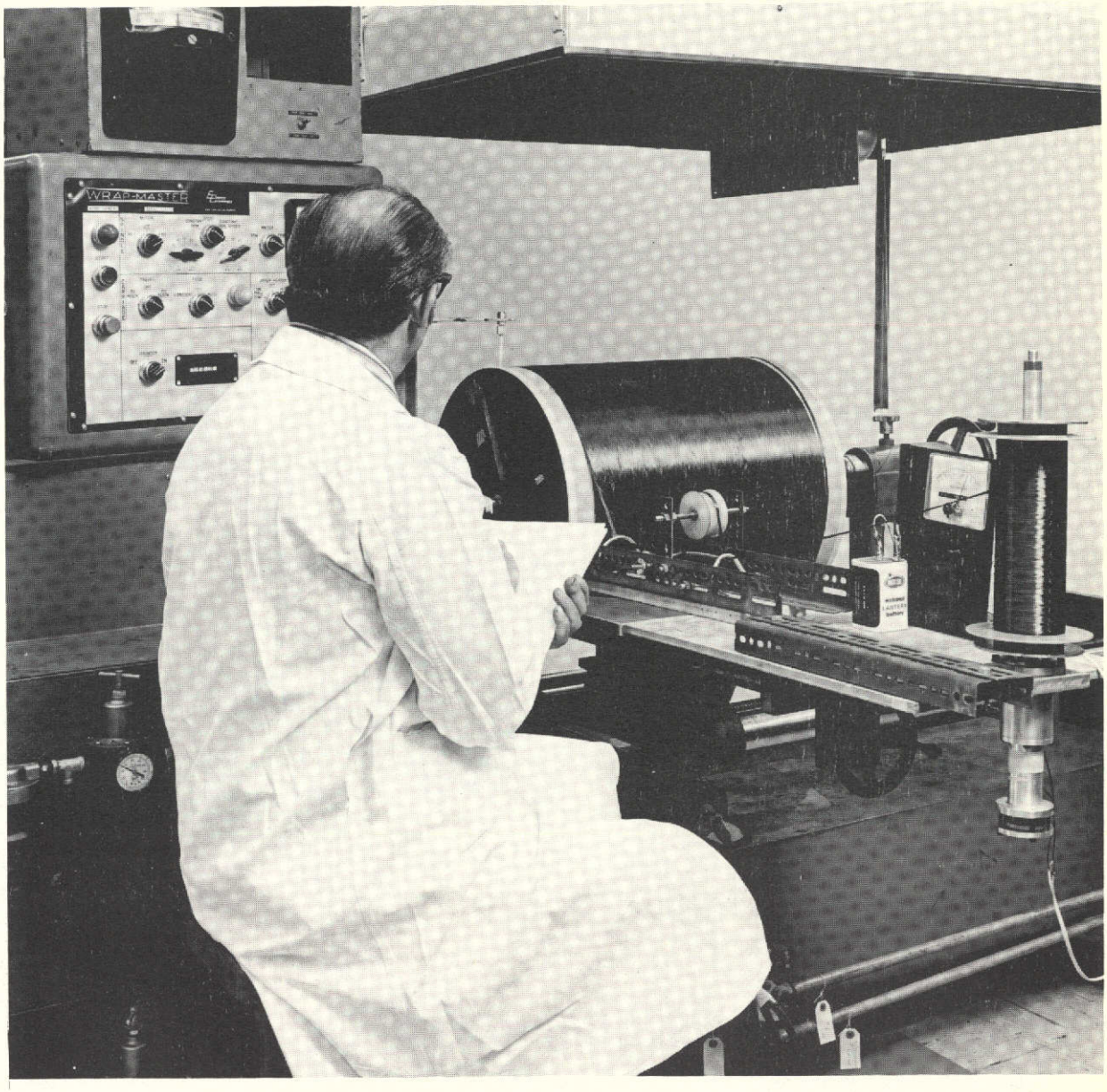


Figure 1 Drum Winding Apparatus

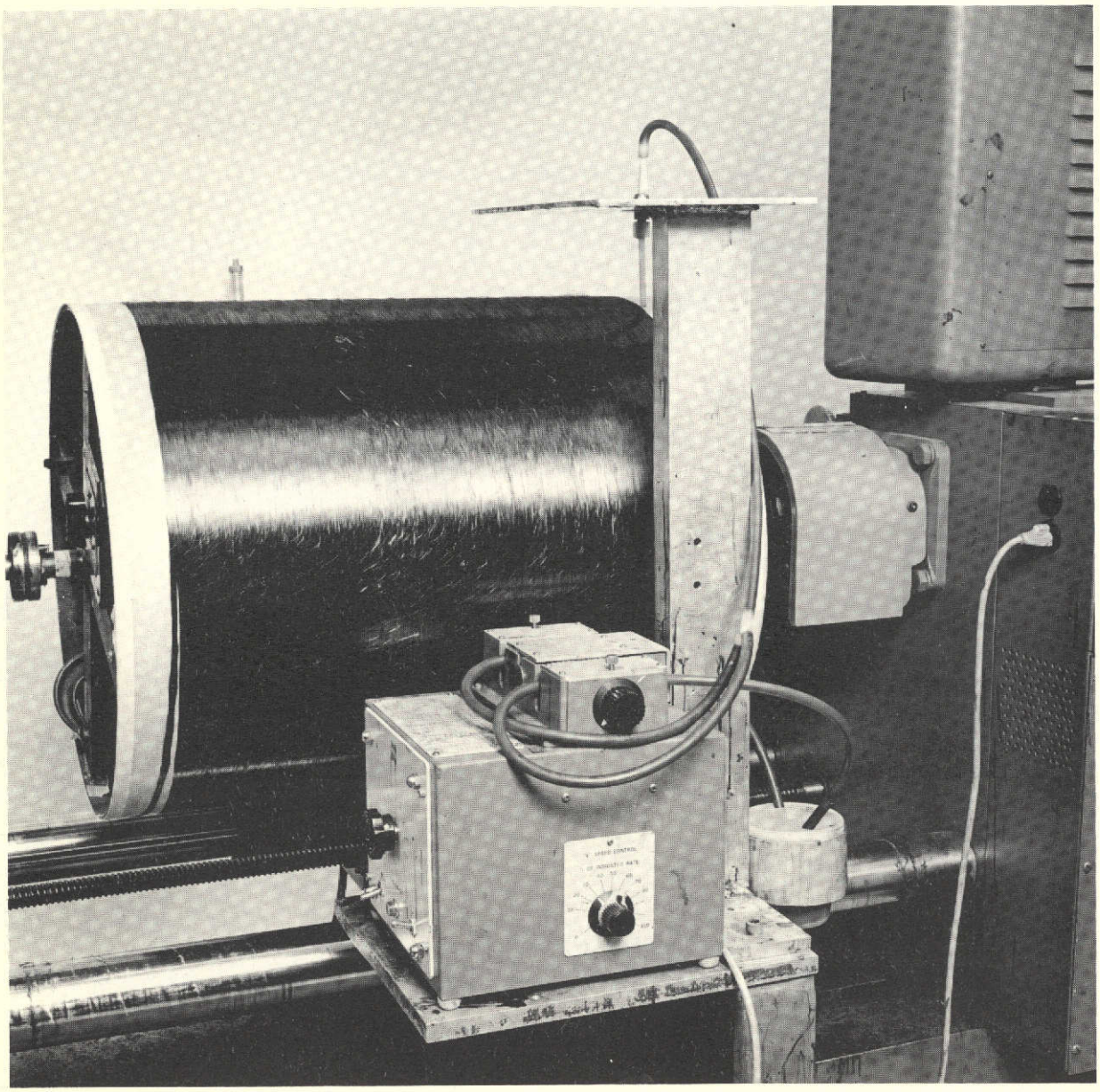


Figure 2 Peristaltic Pump for Metering Monomer Solution Onto Fiber

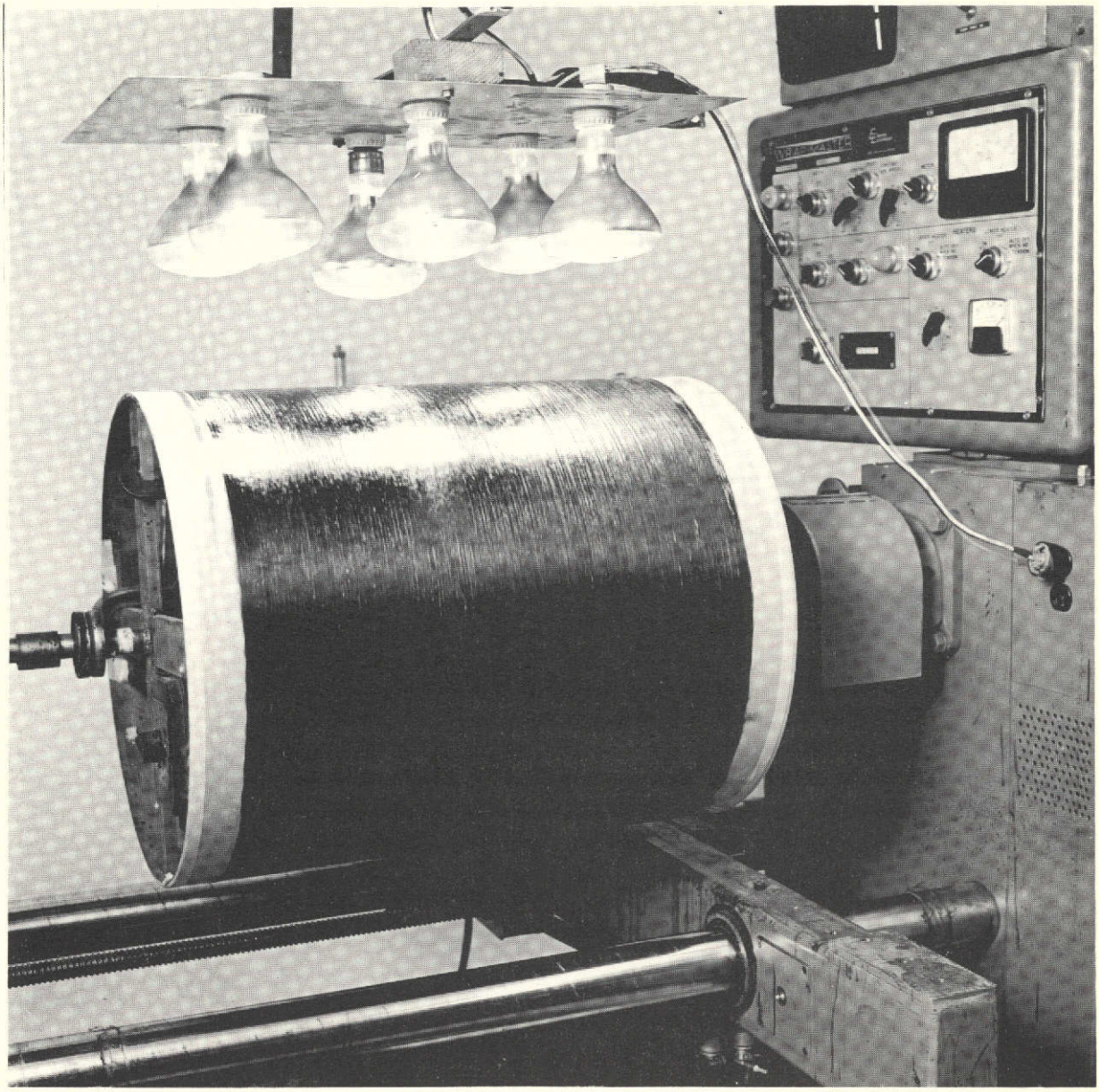


Figure 3 Initial Devolatilization of Prepreg with IR Lamps

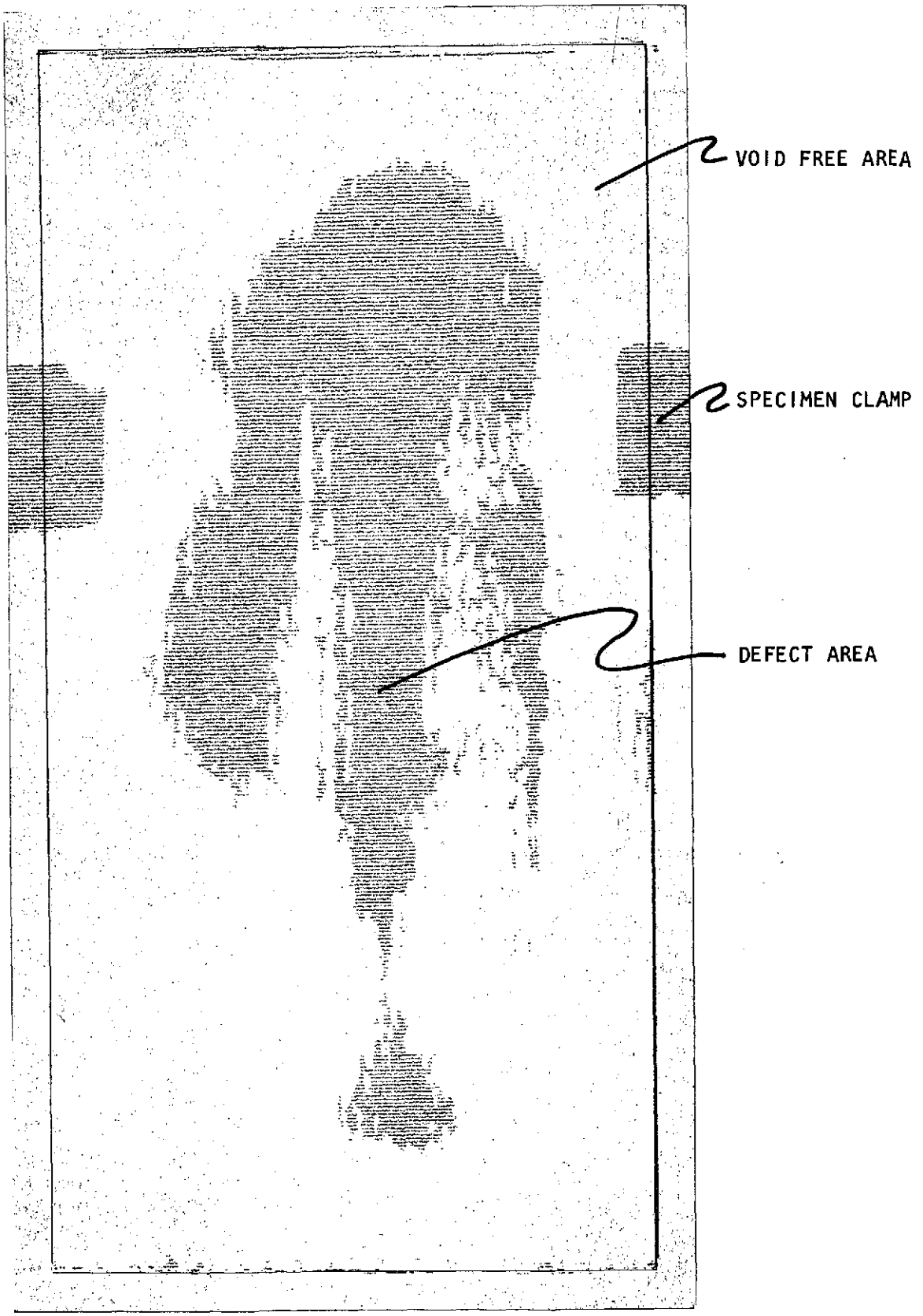
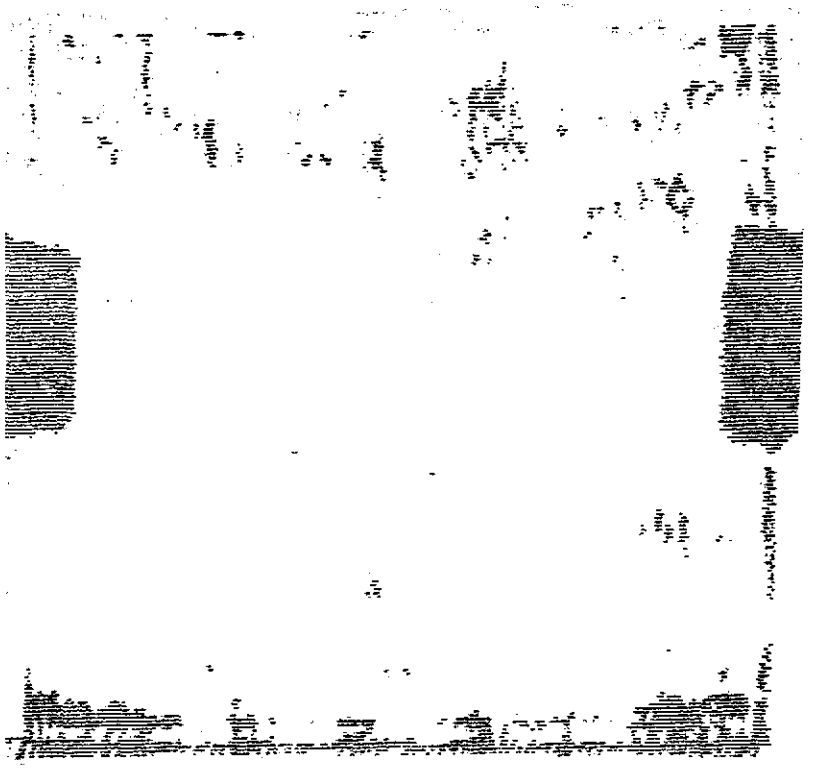


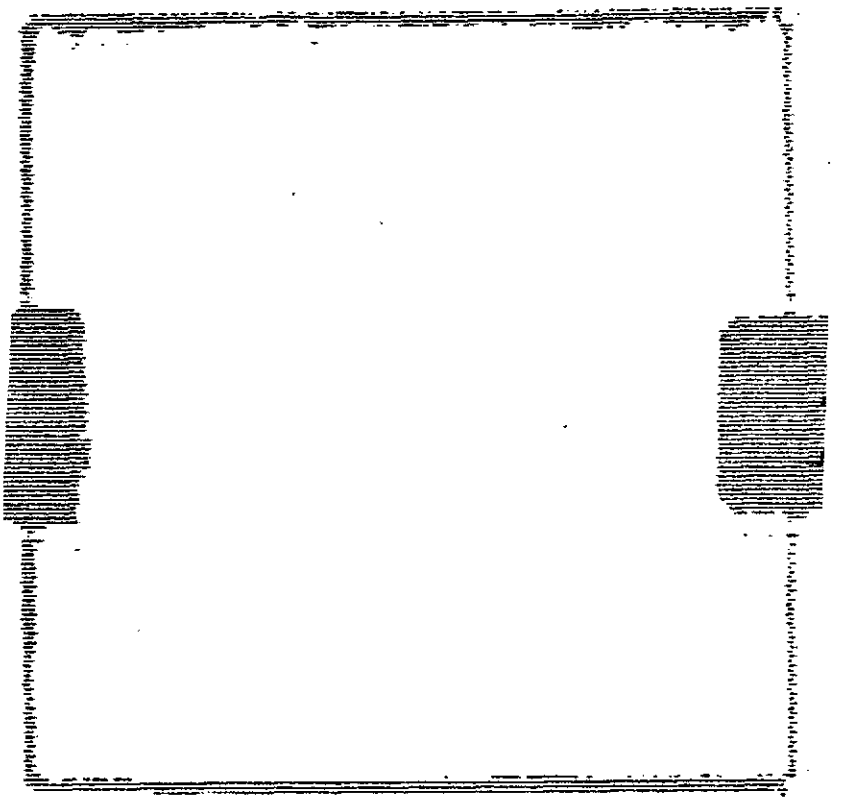
Figure 4 C-Scan of Laminate Molded by the Flow-During-Imidization Process



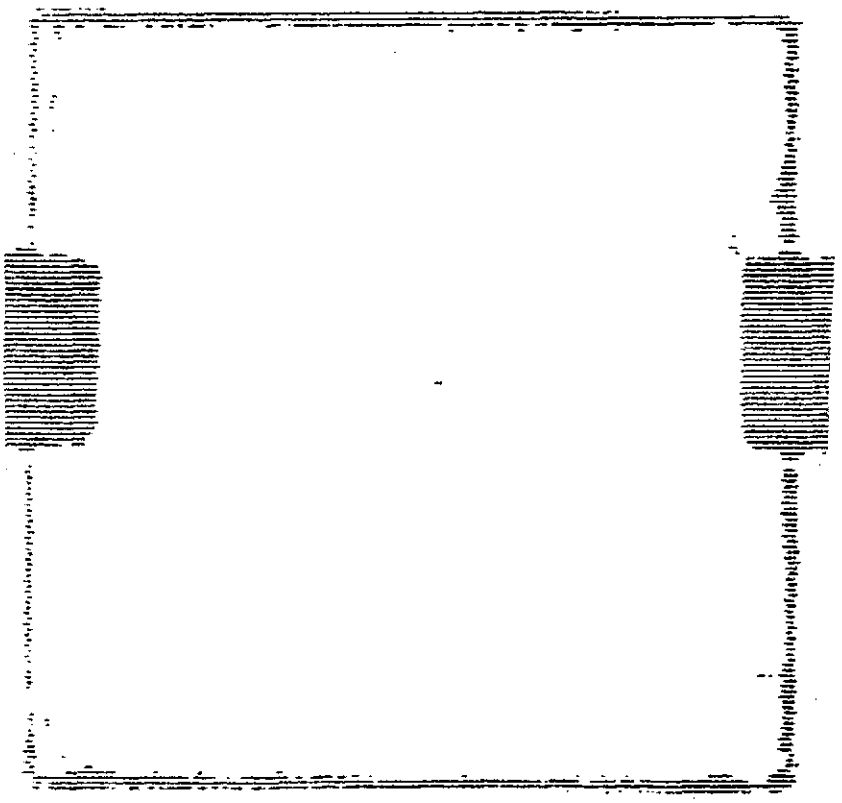
Laminate 701-13: HM-S

Laminate 701-9: HT-S

Figure 5 Sonic C-Scans of HT-S and HM-S Reinforced PMR-15 Laminates with the Same Process Cycle



Laminate 701-14: HM-S



Laminate 701-12: HT-S

Figure 6 Sonic C-Scans of HT-S and HM-S Reinforced PMR-15 Laminates with the Same Process Cycle

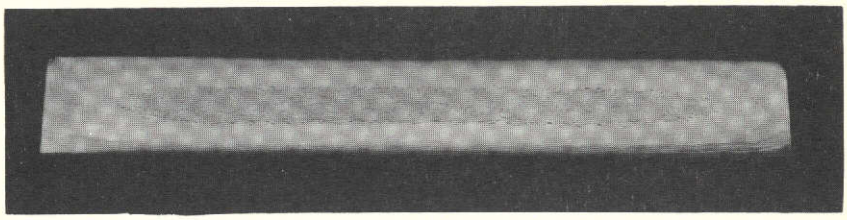


Figure 7 Cross-Section of Unidirectional 10.2 cm x 10.2 cm x 1.5 cm Laminate Showing Porous Center

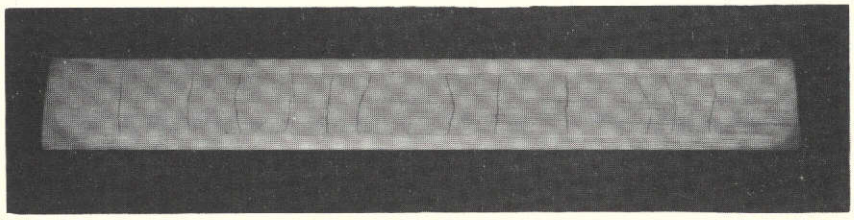


Figure 8 Cross-Section of Cross-Plied 10.2 cm x 10.2 cm x 1.4 cm Laminate

PERCENT WEIGHT LOSS OF PMR-15/HM-S COMPOSITES EXPOSED TO 100 ML/MIN. AIR FLOW AT TEMPERATURES SHOWN

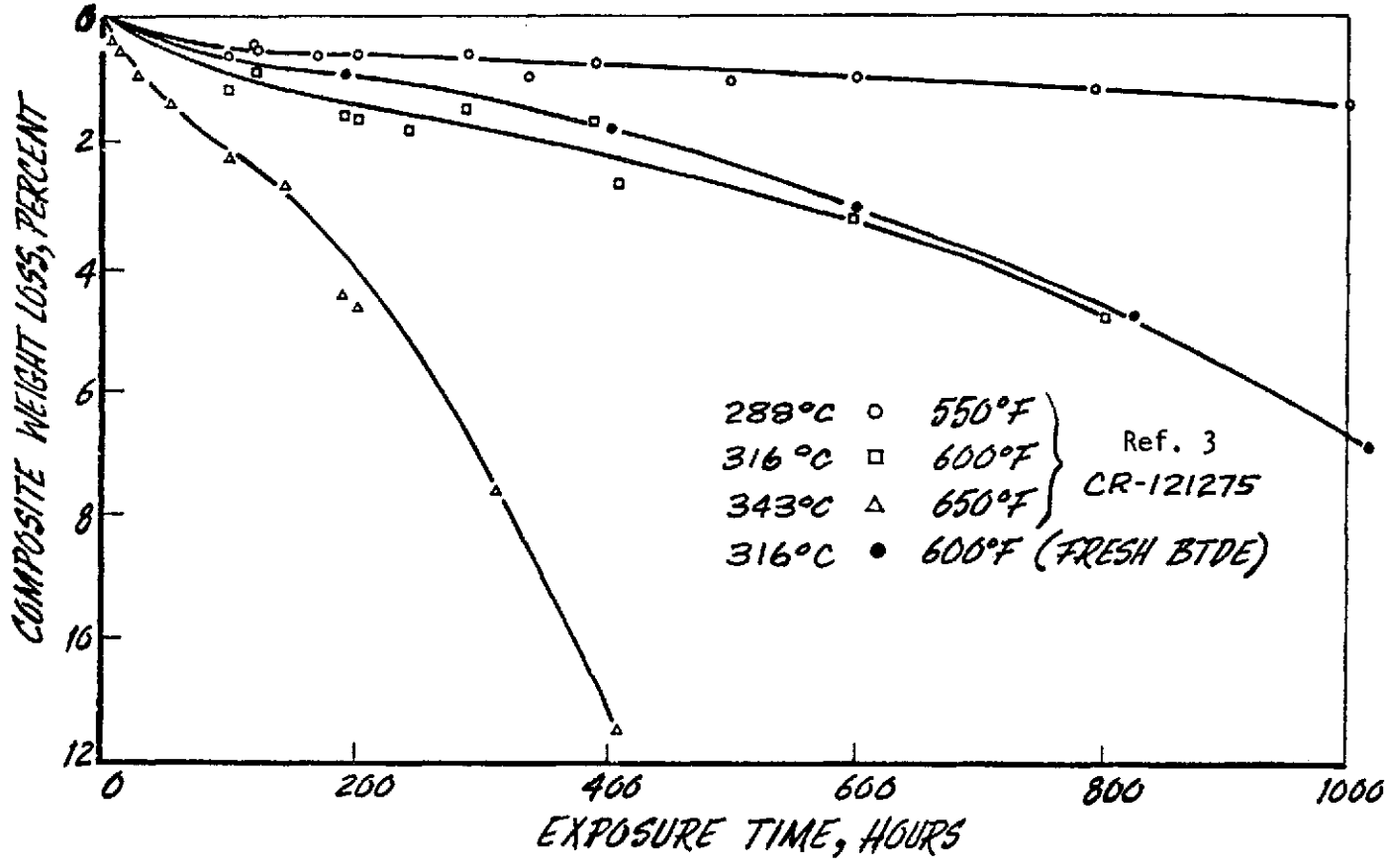


FIGURE 9

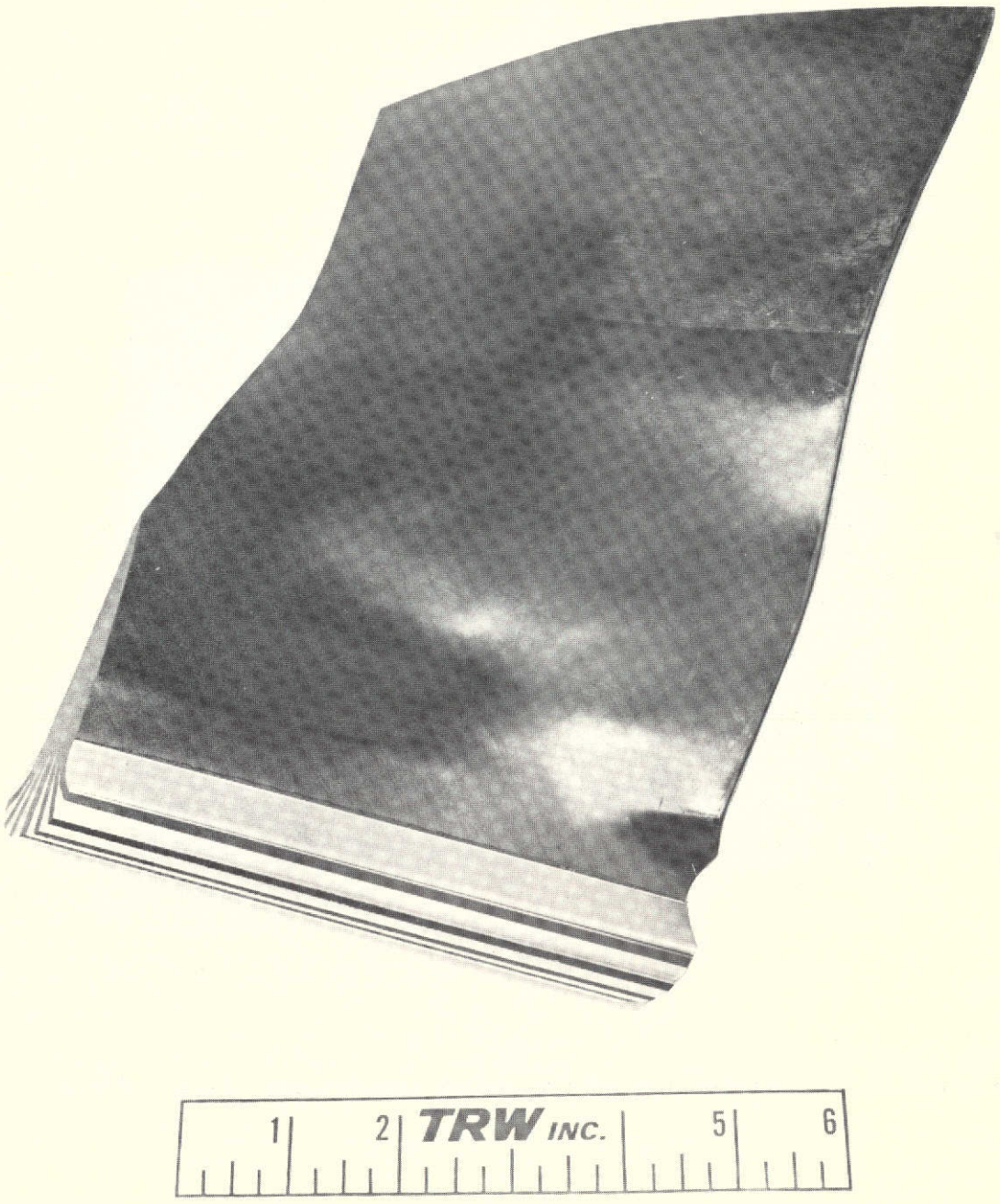
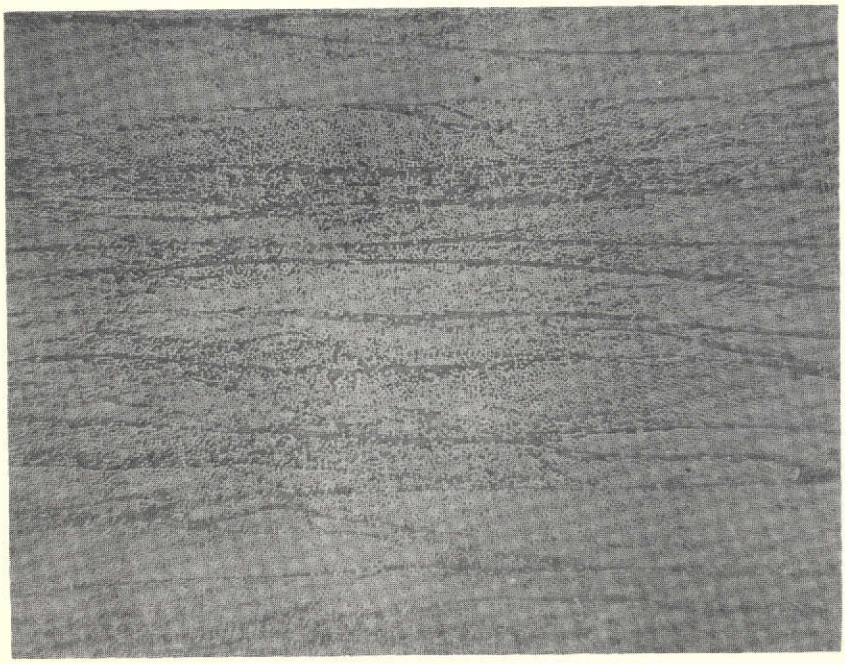
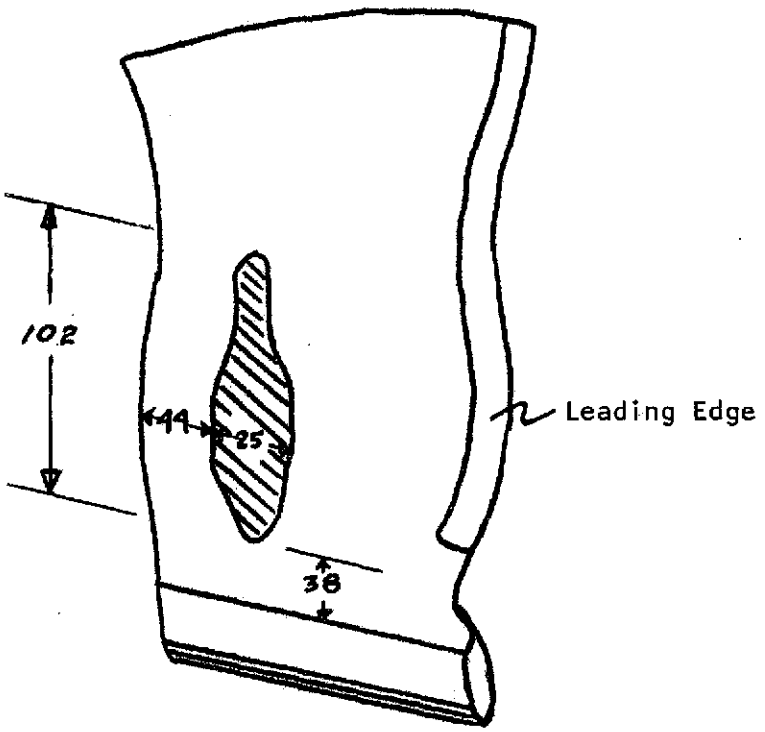


Figure 10 Ultra-High Tip Speed Fan Blade in Finished Machined Form



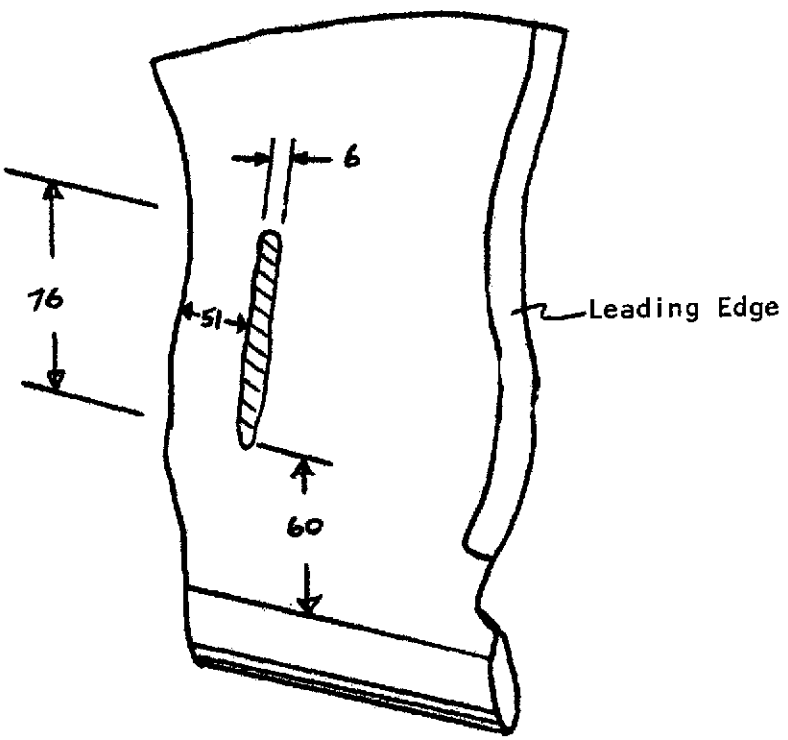
50X

Figure 11 Cross-Section of Center of Low Residual Stress Panel



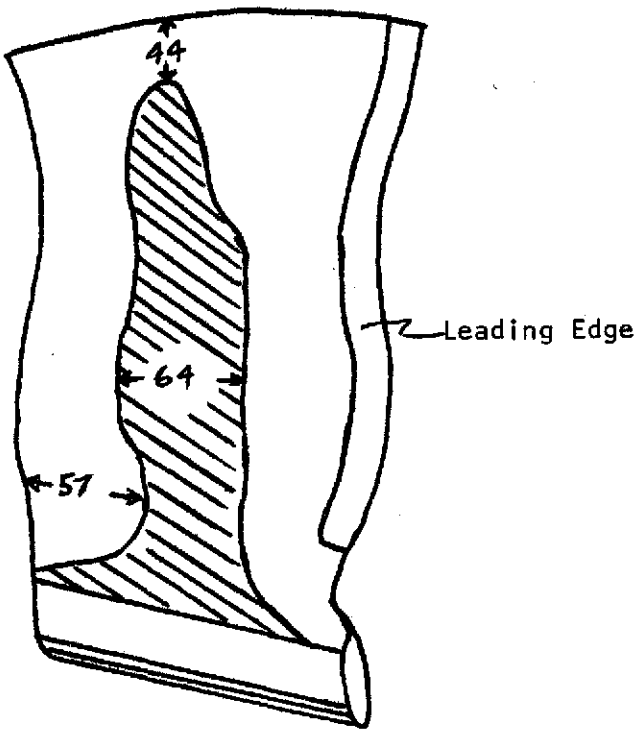
Dimensions in Millimeters

Figure 12 Ultrasonic Indications Shown for S/N T-1 Blade



Dimensions in Millimeters

Figure 13 Ultrasonic Indications Shown for S/N T-2 Blade



Dimensions in Millimeters

Figure 14 Ultrasonic Indications Shown for S/N T-3 Blade

APPENDIX

TEST METHODS

Certain frequently used routine mechanical test methods have not been described in the body of the text. These specimens are shown in the following appendix pages and are widely used and generally accepted. The notes with the sketches are self-explanatory.

Since industry-wide accepted methods are not available for determining internal laminate quality by ultrasonic inspection or for performing isothermal gravimetric analyses, the techniques employed in these two methods are described in greater detail.

ISOTHERMAL GRAVIMETRIC ANALYSIS

Figure A-1 displays the setup in which the isothermal gravimetric analyses were run. The photograph displays the air bottle, flowmeter, specimen stack on a screen and the inner chamber in which air flow was controlled at 100 ml/min. (6.1 in^3/min.). Note that at the bottom of the inner chamber a ring is shown. This is a copper tube, sealed at the end, through which the bottled air was passed; small holes drilled in the copper tube on one inch centers permit an even, regular flow of air up through the chamber. Not shown is a length of copper tubing in the oven designed to preheat the air-to-oven temperature before discharge into the chamber. The bottled air used had a dew point temperature of -59°C (-75°F). The inner chamber had a volume of 1400 x 10^{-5} m^3 (855 cubic inches). Temperatures inside the chamber were monitored with calibrated thermocouples.

ULTRASONIC INSPECTION

A through-transmission method with a C-scan recording was used. The tests were performed at 10 MHZ with a 2.38 mm (3/32 inch) diameter sending crystal of the SL type. The receiving crystal (SIZ) was 12.7 mm (1/2 inch) in diameter. The ultrasonic unit was a Sperry UM-700 with an Automation Industries SR-194 C-Scan recording unit; an HFN pulser was used. While the signal screen height was varied originally from 25 to 75%, it was found that the 50% level displayed good contrast between sound and flawed areas and was used as a general standard throughout all subsequent testing. In making repetitive setups, a 3.17 mm (1/8 inch) thick piece of titanium (6Al-4V) was used as a standard to set screen height at 30%.

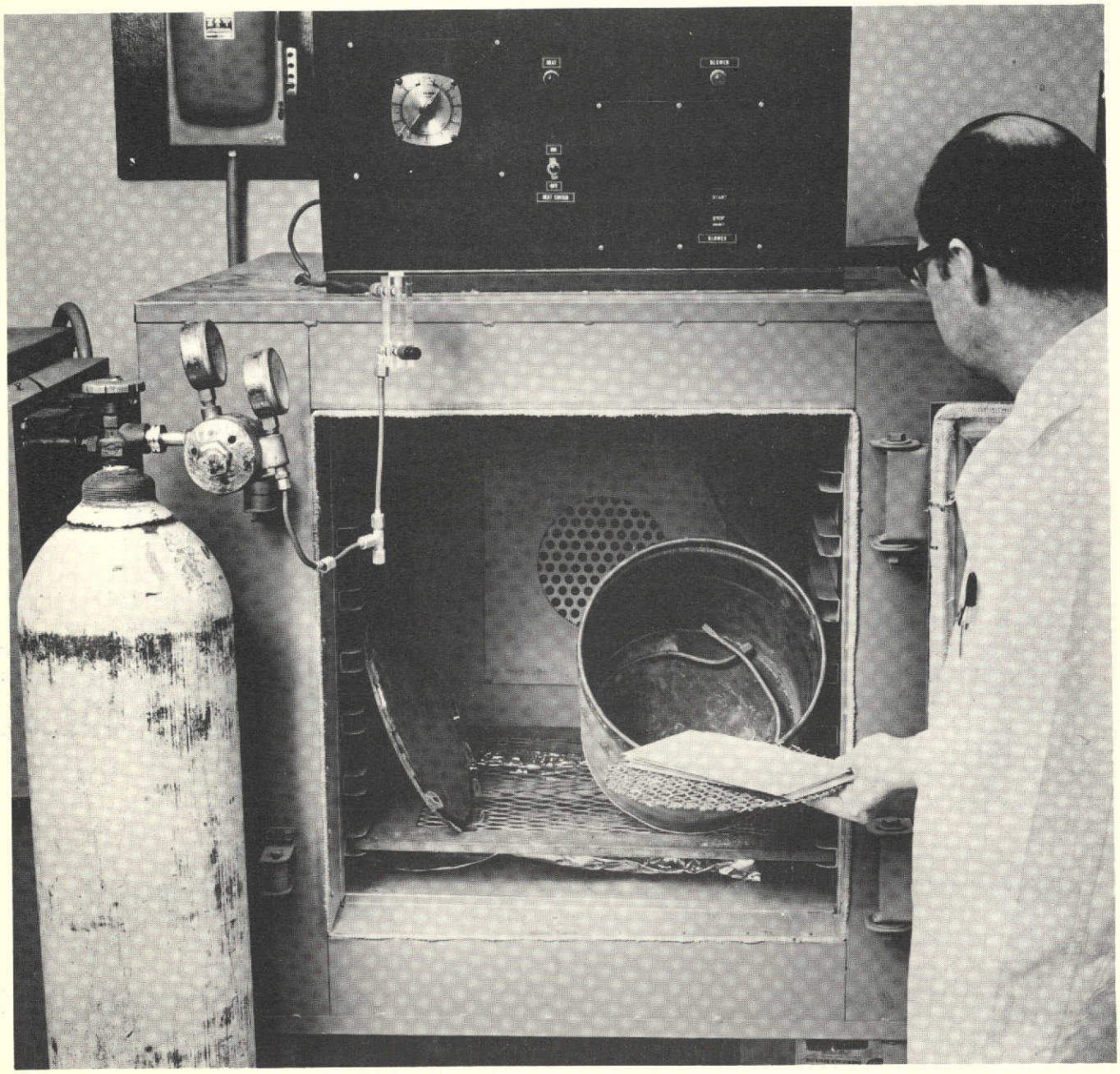


Figure A-1 Isothermal Exposure Set-Up Showing Air Source, Flow Meter and Inner Chamber

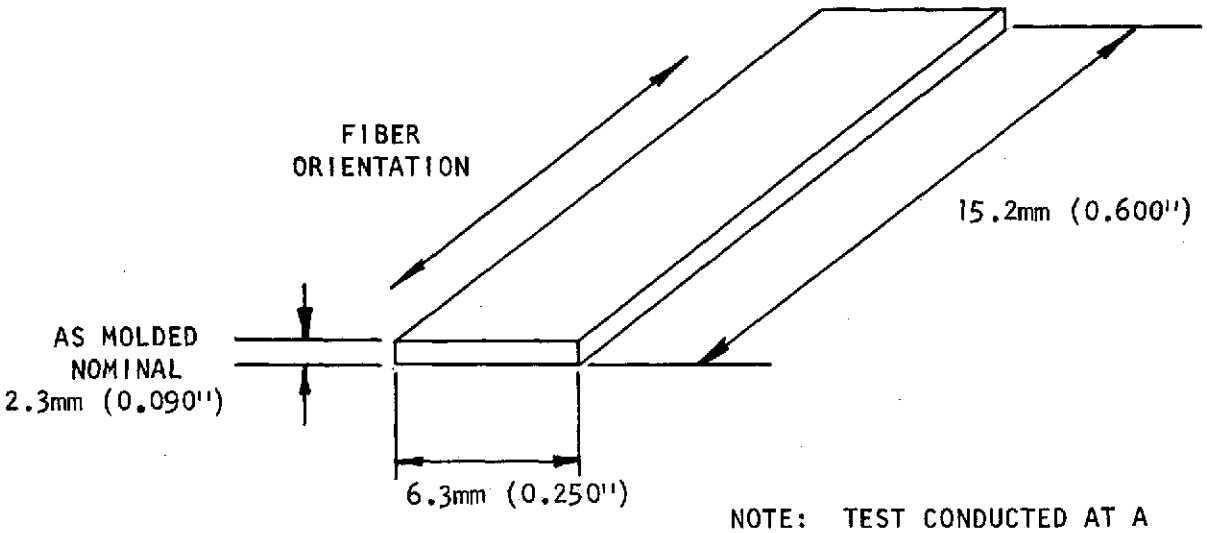


Figure A-2 Short Beam Shear Specimen

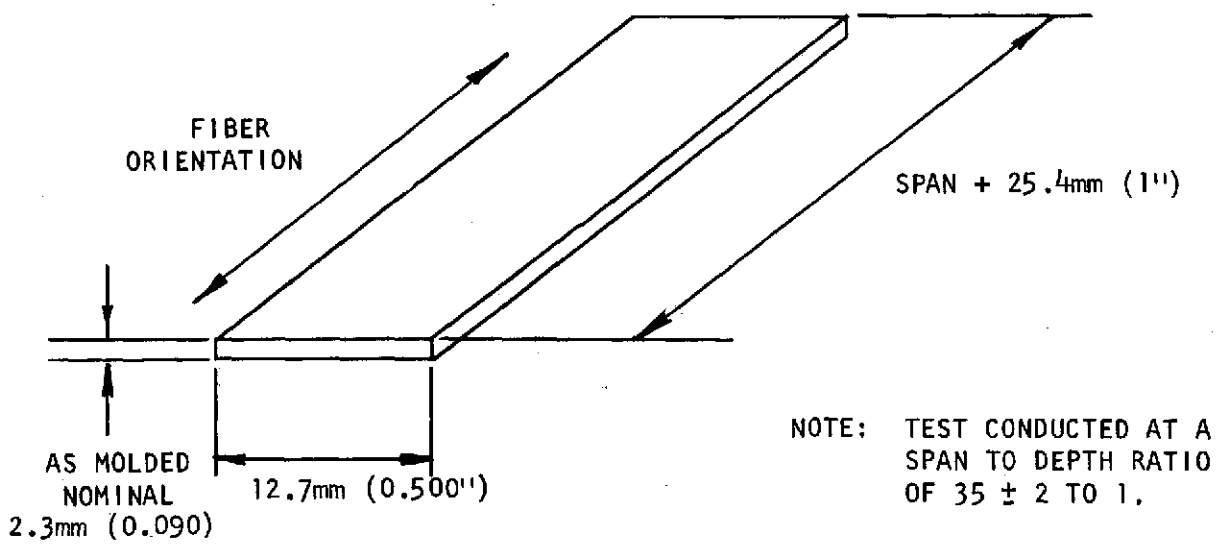
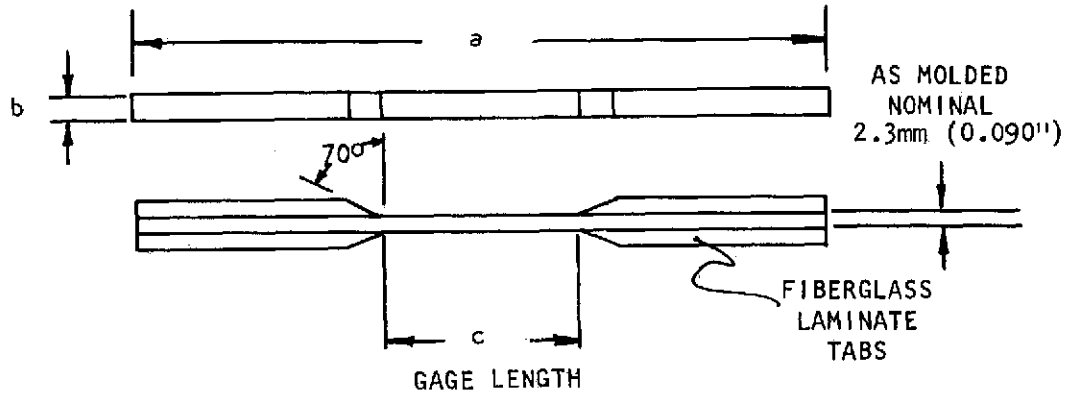


Figure A-3 Flexure Specimen (Three Point)



	0°		CROSS-PLY	
	mm	Inches	mm	Inches
a	152.4	6	203.2	8
b	6.3	1/4	19.0	3/4
c	38.1	1.5	88.9	3-1/2

NOTE: FOR ROOM TEMPERATURE TESTING, EPOXY/FIBERGLASS CLOTH LAMINATE TABS BONDED WITH ROOM TEMPERATURE CURING EPOXY ADHESIVE.

Figure A-4 Cross-Ply and 0° Tensile Specimens

REFERENCES

1. Serafini, T. T., Delvigs, P., Lightsey, G. R., "Thermally Stable Polyimides from Solutions of Monomeric Reactants," NASA Technical Note TN D-6611, January 1972.

2. Serafini, T. T., Delvigs, P., and Vannucci, R. D., "In Situ Polymerization of Monomers for Polyphenylquinoxaline/Graphite Fiber Composites," Society of Plastics Industry Conference, Washington, D.C., February 4-8, 1974.

3. Cavano, P. J., "Resin/Graphite Fiber Composites," NASA CR-121275, March 15, 1974.

4. Hanson, M. P. and Serafini, T. T., "Effects of Thermal and Environmental Exposure on the Mechanical Properties of Graphite/Polyimide Composites," SAMPE Conference, October 1971.

5. Haynes, W. M. and Tolbert, T. L., Journal of Composite Materials, "Determination of the Graphite Fiber Content of Plastic Composites," Vol. 3, October, 1969, pp. 709-712.

6. Serafini, T. T. and Vannucci, R. D., "Tailor Making High Performance Graphite Fiber Reinforced PMR Polyimides," NASA TMX-71616.